ENTHALPIES AND ENTROPIES OF ION–EXCHANGE REACTIONS

By J. F. Duncan*

Summary

By use of exchange isotherms determined at different temperatures, the chemical potentials and partial molar heats and entropies of the sodium-hydrogen ion-exchange reaction on a sulphonated polystyrene exchanger are evaluated. These show that both species are almost completely ionized in the exchanger, and very similar to their states in aqueous solution. In the high concentrations obtainable in the exchanger, however, there is some cation-cation interaction, which is practically linear with composition. A similar treatment of the barium-hydrogen system indicates that there is some interaction between the barium ion and the resinate structure.

I. Introduction

It has previously been shown (Duncan 1952 ; Glueckauf 1952) that a large number of experimental facts can be unified if one regards an ion exchanger of the sulphonated polystyrene type unreservedly as an aqueous electrolyte (e.g. sodium " resinate ") dissolved in the swelling water which the exchanger contains. Osmotic and activity coefficients can then be unambiguously evaluated from experiments with single-ion systems and used to predict distribution coefficients. In spite of this success, there still remains a number of phenomena which cannot be adequately explained. Some of them are discussed in the present paper, in which some earlier experimental data are reassessed.

II. Deviation from Theory of Simple Ion-Exchange Systems

Treatment of an ion exchanger as if it were an aqueous solution of the exchanging ions leads to agreement of the calculated distribution constants with experiment only for exchangers of low cross-linking (Glueckauf 1952). At higher cross-linking the experimental mass-product is found to pass through a maximum and even to decrease, whereas the theoretical values always increase with increasing degree of saturation by the more strongly adsorbed ion. This may be seen by inspection of Figure 1, in which the theoretical values have been calculated as described earlier (Glueckauf 1952), assuming osmotic coefficients for the pure hydrogen and sodium resinates at the appropriate molality and the corresponding value of the swelling pressure. The experimental data are from the work of Reichenberg, Pepper, and McCauley (1949). The difference between the theoretical and experimental curves is a measure of the excess Gibbs free energy of the ions in the exchanger. A plot of this term for different degrees of cross-linking is shown in Figure 2. The theoretical and practical results are

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in as close agreement as can be expected at the hydrogen-saturated end of the
isotherm especially with extremely highly cross-linked exchangers. (Such
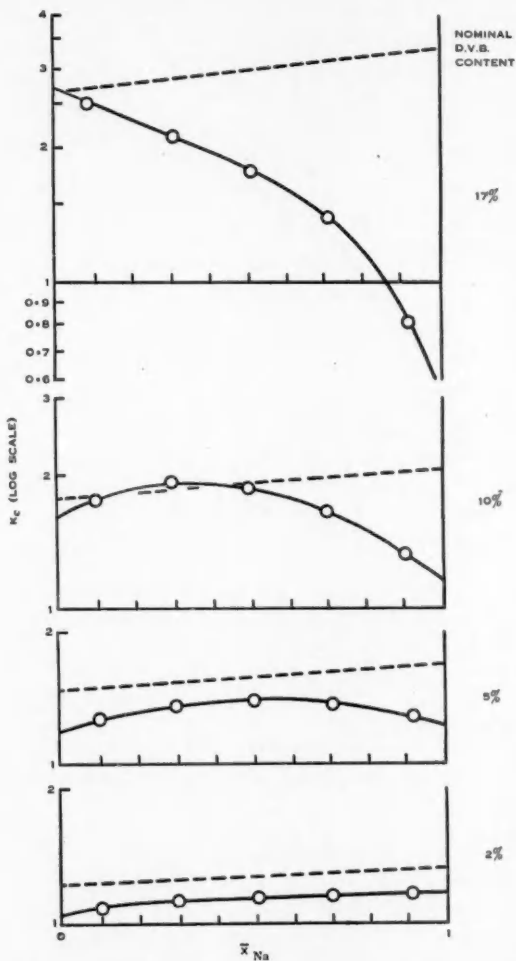deviations as there are could be accommodated by errors in the swollen resin

Fig. 1.—Predicted and experimental mass-product plots for
sodium-hydrogen systems.
       —— Experimental values (Reichenberg, Pepper, and
             McCauley 1951).
       .... Theoretically predicted values.
The percentage nominal D.V.B. content of the exchanger is
indicated.

volume and concentration, and more refined work would be necessary to ascertain whether they are real.) Nevertheless, the closeness of the experimental and theoretical curves means that the sodium " resinate " activity coefficient is almost the same in trace concentrations ($\overline{X}_{Na}=0$) as in a sodium-saturated exchanger at constant ionic strength even in concentrations of 10–15 molal. It will be seen later that this agreement is fortuitous, and must be ascribed to the cancellation of two trends tending to alter the activity coefficient of the sodium ion in opposite directions, probably the following. Interaction which occurs between the sodium ion and the hydrogen ion (either directly or indirectly) will tend to depress the activity of the former (see below). But, as the concentration of sodium ions is decreased, the activity coefficient would normally be expected to rise (as it does with ordinary electrolytes of analogous type in
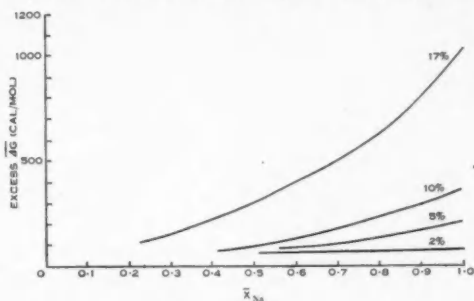

Fig. 2.—Excess Gibbs function for sodium-hydrogen exchange. (The nominal percentage D.V.B. content of the exchanger is indicated.)

aqueous solution when replaced at constant ionic strength with electrolytes of high activity coefficient). Specific interaction between the sodium and hydrogen ions must thus be sufficiently strong to cancel out the expected increase in free energy of the sodium ion at the hydrogen-saturated end of the isotherm.

Consider, now, the sodium-saturated end of the isotherm of Figure 1. The fact that the observed and theoretically-calculated values of the distribution coefficient may differ by as much as 80 per cent. implies that some assumption in the theoretical treatment is in error. One possible explanation is that, as $\overline{X}_{Na}$ increases, the sodium ion becomes partly ion-paired, or covalently-bound with the resinate structure. This is a very likely occurrence for silver and barium ions (see later), but is intrinsically unlikely with either sodium or hydrogen ions. Further, for this to be the explanation, the calculated value of the mass product would have to be less than the experimentally obtained value, whereas in fact it is greater. Also, consider how $\overline{\gamma}_{HX}$ and $\overline{\gamma}_{NaX}$ would vary in the equation

$$K_c = \frac{[\overline{Na}^+]}{[\overline{H}^+]} \times \frac{\{H\}}{\{Na\}} = \left[\frac{\overline{\gamma}_{HX}}{\overline{\gamma}_{NaX}}\right]_{I=[\overline{Na}^+]+[\overline{H}^+]}, \quad \dots\dots\dots (1)$$

where X is the common anion and I is the ionic strength. If there were no change in the water content of the exchanger, then by analogy with aqueous

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electrolytes both $\bar{\gamma}_{HX}$ and $\bar{\gamma}_{NaX}$ would be expected to decrease with increasing sodium ion fraction $\bar{X}_{Na}$. It follows, therefore, that $\bar{\gamma}_{HX}$ decreases more quickly with $\bar{X}_{Na}$ than does $\bar{\gamma}_{NaX}$. In other words, either sodium tends to become more ionic (as the exchanger becomes sodium-saturated), or the hydrogen becomes less ionic than would be expected from aqueous solutions of comparable concentrations. This conclusion is not affected by variations in the water content of the exchanger, although its validity is a little more difficult to verify.

These conclusions show that some further development of theory is necessary. By evaluating the partial thermodynamic functions of the ion-exchange system, supplementary information about the state of the ions in the exchanger can be obtained without any specific assumptions about the osmotic and activity coefficients of the exchanger itself.

III. Evaluation of Partial Thermodynamic Quantities

In deriving thermodynamic functions from experimental data for an ion-exchange equilibrium, it has been customary to evaluate a Gibbs free energy,

$$\overline{\Delta G}_c = RT \ln K_c, \qquad \dots\dots\dots\dots \quad (2)$$

and the corresponding enthalpies and entropies. Some arbitrary assumption for the activities of the ions in the exchanger phase must be made to do this, although in the case of exchange between ions of the same valency type the value of $\overline{\Delta G}_c$ is the same for any assumption which is reasonable. Nevertheless, the quantities obtained are not independent of the nature of the resin phase and, further, they refer to the overall exchange reaction.

But, suppose we have an ion exchanger in equilibrium with a solution of two uni-univalent electrolytes MX and NX with a common anion. Then the work required to transfer 1 mole of the electrolyte MX from a solution at infinite dilution into the exchanger is

$$\overline{\Delta G} = RT \ln \{MX\}, \qquad \dots\dots\dots\dots \quad (3)$$

where $\{MX\}$ is the activity of MX in the aqueous mixture external to the ion exchanger. Knowing the value of $\overline{\Delta G}$ at two temperatures, we can then calculate the partial molal entropy and heat content terms, namely,

$$[\overline{\Delta S}]_{\overline{MX}} = -\left[\frac{\partial(\overline{\Delta G})}{\partial T}\right]_{\overline{MX}} = -R \ln \{MX\} - RT\left[\frac{\partial \ln \{MX\}}{\partial T}\right]_{\overline{MX}}, \quad \dots \quad (4)$$

and

$$[\overline{\Delta H}]_{\overline{MX}} = [T\overline{\Delta S}]_{\overline{MX}} + [\overline{\Delta G}]_{\overline{MX}}. \qquad \dots\dots\dots\dots \quad (5)$$

Note that the differentiations are made at constant $\overline{MX}$. This is analogous to the usual procedure in gaseous sorption, where the differential heats and entropies are determined by the appropriate differentiation, at constant surface coverage, of

$$\overline{\Delta G} = RT \ln p, \qquad \dots\dots\dots\dots \quad (6)$$

where p is the pressure of gas. The concentration of anion in the exchanger is normally very small when the solutions are dilute, and therefore for practicable

purposes we may assume the above differentiations to be performed at constant M, that is, at a given degree of saturation of the exchanger with the ion M. The evaluated quantities then give direct information about the thermodynamic properties of the resin phase without any restricting assumptions. Here, we do not make any postulates about the degree of ionization of the " resinate ", the degree of cation-cation or cation-anion interaction. But it will be seen later that information of this type can be adduced from the magnitude of the thermodynamic quantities.

IV. Evaluation of Partial Thermodynamic Quantities for the Sodium-Hydrogen System

To evaluate the free energy term

$$\overline{\Delta G} = 2RT \ln [\text{NaCl}] (\gamma^{\pm})_{\text{NaCl}}, \qquad \dots\dots\dots\dots \quad (7)$$

and the corresponding heats and entropies for the sodium-hydrogen exchange system in chloride solutions it is necessary to know the mean molal ionic activity coefficients $\gamma^{\pm}_{\text{NaCl}}$, $\gamma^{\pm}_{\text{HCl}}$ in the external mixed solution at the two temperatures at which the exchange isotherm was determined. These are not available in the literature. One therefore assumes (i) that the activity coefficients are independent of temperature and (ii) that $\gamma^{\pm}_{\text{NaCl}}$ and $\gamma^{\pm}_{\text{HCl}}$ in binary mixtures of the two electrolytes may be evaluated by application of the Harned rule (Harned and Owen 1950). Both these assumptions are unobjectionable over a restricted temperature and concentration range. Hence, $\overline{\Delta G}$, $\overline{\Delta H}$, and $T\overline{\Delta S}$ were evaluated for both the sodium chloride and hydrochloric acid using experimental results reported earlier (Duncan and Lister 1949a). The latter two functions plotted against $\overline{X}_{\text{Na}}$, the proportion of sodium ions in the exchanger, are shown in Figures 3 and 4. Table 1 gives the experimental values from which the thermodynamic functions were calculated.

(a) The Partial Molal Enthalpies (Fig. 3)

First consider the sodium ion. It will be noticed that $\overline{\Delta H}_{\text{Na}}$ is negative and becomes less negative as the proportion of sodium in the exchanger increases. In other words, the sodium ions are more coordinated (either with water molecules or with anions) when they are present in trace amounts, and less when in macro-amounts. On the other hand, the reverse seems to be the case for the hydrogen ion, for which $\overline{\Delta H}_{\text{H}}$ becomes less positive (more negative) as the amount of hydrogen in the exchanger increases, that is, hydrogen ions are more ion-paired in low hydrogen concentrations. This is in accordance with Section II. The energies involved are small and the variation from one end of the isotherm to the other is clearly not great enough to modify the conclusion in Section I that the ionic species are effectively completely ionized over the whole range. In the case of the hydrogen ion, the trend seems a little surprising, as one would hardly expect $\overline{\Delta H}_{\text{H}}$ to decrease in this way merely by interaction with sodium ions. But interaction between the hydrated hydrogen ion and the resinate structure

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TABLE 1

EVALUATION OF THERMODYNAMIC FUNCTIONS FROM EXPERIMENTAL DATA FOR Na/H EXCHANGE

The absolute accuracy is indicated by the number of significant figures, except for ΔH_H, for which the figures indicate only relative values and the absolute accuracy is only ± 2 per cent.

$\bar{X}_{Na}$	$(X_{Na})_{20}$	$(X_{Na})_{87}$	$\{NaCl\}_{20}$	$\overline{\Delta G}_{Na} = 2RT$ $\times \ln[\{NaCl\}](\gamma\pm)_{NaCl}$	$\overline{\Delta H}_{Na}$	$(T\Delta S)_{Na}$	$\{HCl\}_{20}$	$\overline{\Delta G}_H = 2RT$ $\times \ln[\{HCl\}](\gamma\pm)_{HCl}$	$\overline{\Delta H}_H$	$(T\Delta S)_H$
0·05	0·034	0·037	0·00446	−6380	−1270	5110	0·151	−2220	292	2510
0·10	0·058	0·074	0·00858	−5640	−1520	4120	0·143	−2300	234	2530
0·20	0·129	0·154	0·0191	−4680	−1110	3570	0·135	−2360	175	2540
0·30	0·215	0·246	0·0321	−4060	−848	3210	0·129	−2420	248	2660
0·40	0·301	0·342	0·0450	−3680	−804	2670	0·107	−2610	380	3090
0·60	0·504	0·552	0·0810	−2740	−572	2170	0·0705	−3140	596	3740
0·80	0·734	0·772	0·111	−2600	−322	2280	0·0404	−3780	920	4700

would be most likely to occur when the ionic strength is relatively high, and the water available for hydration is relatively low (i.e. at the sodium-saturated end of the isotherm). This would lead to a $\overline{\Delta H}_H$ variation in the sense observed.
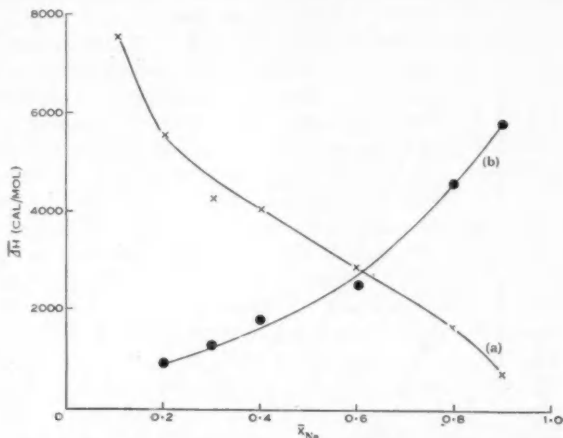

Fig. 3.—Partial molal heats for sodium chloride and hydrochloric acid in the sodium-hydrogen exchange reaction on " Dowex 50 ".

(a) Sodium (negative).   (b) Hydrogen (positive).

Such an effect would also predominate in exchangers of high concentration (cross-linking) which would account for the more steeply falling values of K_c with increase of $\overline{X}_{Na}$ (Reichenberg, Pepper, and McCauley 1951).
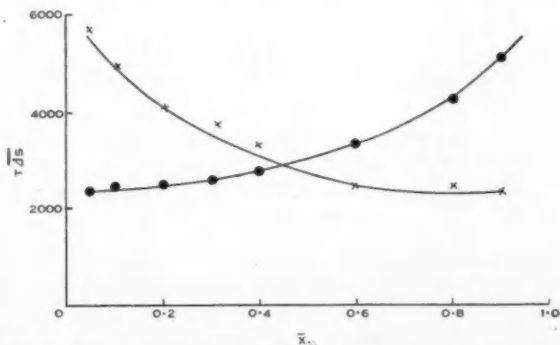

Fig. 4.—Partial molal entropies of sodium chloride and hydrochloric acid in the sodium-hydrogen exchange reaction on " Dowex 50 ".

× Sodium.   ● Hydrogen.

(b) The Partial Molal Entropies (Fig. 4)

If there were no special interaction between the different ions, that is, if the partial molal heats were independent of the proportions of sodium and hydrogen ions present, the total configurational entropy would be given by

$$\bar{S}^c = R \ln \left[\frac{(N_H + N_{Na})!}{N_H! N_{Na}!} \right], \quad \dots\dots\dots\dots \quad (8)$$
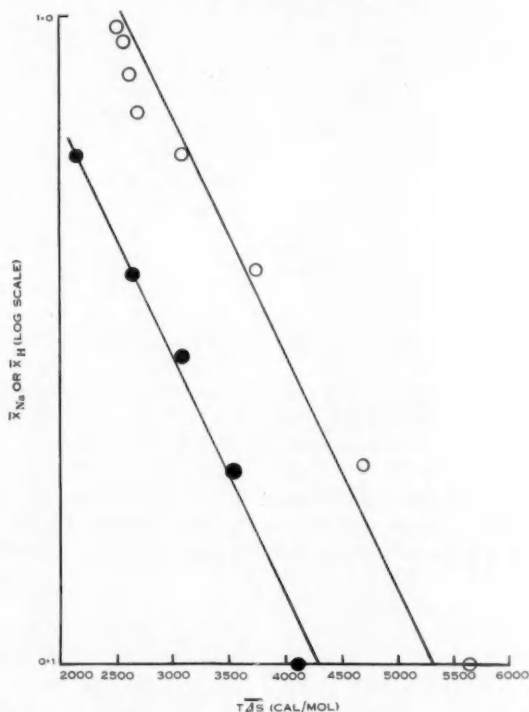

Fig. 5.—Variation of partial molal entropies of sodium-hydrogen exchange reaction with resin composition.

○ Sodium.   ● Hydrogen.   The lines are drawn with the theoretical slope.

where N_H and N_{Na} are the numbers of hydrogen and sodium ions respectively present in the mixture. Applying Stirling's approximation to this expression and differentiating, we obtain the equations

$$\overline{\Delta S}_H^c = -R \ln \bar{X}_H, \quad \dots\dots\dots\dots \quad (9)$$
$$\overline{\Delta S}_{Na}^c = -R \ln \bar{X}_{Na}, \quad \dots\dots\dots\dots \quad (10)$$

for the configurational contributions to the partial molal entropies. These would be the only variable parts of the entropies, so that we might expect the

curves of $\overline{\Delta s}_H$ against $\ln \bar{X}_H$ and of $\overline{\Delta s}_{Na}$ against $\ln \bar{X}_{Na}$ to be linear. This is in fact so, as Figure 5 shows. The slopes of the curves there are actually $-2RT$, since the quantities calculated include contributions from the chloride ions.

We have, however, seen that there certainly is some specific interaction between the ions, that is, that the interaction energy between two hydrogen ions in the resin is not the same as that between two sodium ions, or between a sodium and a hydrogen ion. One effect of this would be that in a mixture of ions there would be a preferential grouping of ions in order to obtain the configuration of lowest energy. Equation (8), which is based on the assumption of a random distribution of ions, would then not hold. This is not a serious objection, however, since in ordinary liquid mixtures the correction necessary is usually small compared with others that must be made. The most important additional correction expected is that due to the changing influence of the surroundings on the vibrational properties of each ion. In liquid mixtures this is important, because the molecules are closely packed, but in ionic solutions and ion-exchange resins it will probably not be so, since the ions will be considerably further apart and the non-Coulomb interactions will be small. Thus it is not surprising to find that the ideal configurational entropy describes all the variation in the partial molal entropies. It is therefore reasonable to conclude that the entropy contributions to the Gibbs free energy do not account for the deviations from ideal behaviour already mentioned. Any deviations observed must be ascribed to the variation of the partial molal heats, which can only be the result of some specific interaction between the ions.

(c) The Heats and Entropies of Exchange

Consider, now, the relation between the partial thermodynamic quantities defined above, and the heats and entropies of exchange evaluated from a measure of the free energy $\overline{\Delta G}_c$, defined in terms of the mass-product as in equation (2). From equations (9) and (10), the overall entropy of exchanging 1 mole of sodium chloride for 1 mole of hydrochloric acid at infinite dilution is

$$\overline{\Delta s}_T = -R \ln \left[\frac{\bar{X}_{Na}}{1 - \bar{X}_{Na}} \right] = \overline{\Delta s}_{Na} - \overline{\Delta s}_H. \quad \ldots \ldots \ldots (11)$$

Now in equation (11) one merely assumes that the two species are in a similar state without specifying whether they are ionic or covalently bound to the resin. If we evaluate the apparent heats and entropies of the reaction from equation (2), we have

$$[\overline{\Delta s}_c]_{\bar{X}_{Na}} = -\left[\frac{\partial(\overline{\Delta G}_c)}{\partial T} \right]_{\bar{X}_{Na}} = -\frac{\partial}{\partial T} \left[RT \ln \left\{ \frac{\bar{X}_{Na}}{1 - \bar{X}_{Na}} \times \frac{\{HCl\}}{\{NaCl\}} \right\} \right]_{\bar{X}_{Na}} ,$$

$$= -R \ln \left\{ \frac{\bar{X}_{Na}}{(1 - \bar{X}_{Na})} \right\} - \left[\frac{\partial(RT \ln \{HCl\})}{\partial T} \right]_{\bar{X}_{Na}} + \left[\frac{\partial(RT \ln \{NaCl\})}{\partial T} \right]_{\bar{X}_{Na}}$$

$$= \overline{\Delta s}_T + \overline{\Delta s}_H - \overline{\Delta s}_{Na}. \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (12)$$

Hence it follows that for a simple ion-exchange reaction for which the interaction forces between the different types of cation and the fixed ionic structure are substantially the same the configurational contribution to the apparent free energy of exchange should be zero. In the case of the sodium-hydrogen exchange, it is remarkably small, not more than 2 cal/mol/°C (see Fig. 6). We must therefore conclude that the changes in the interaction between the ions are not sufficiently great to affect the partial entropy of the exchange reaction, which is much less sensitive to such changes than the partial heat. Further, it follows that to a first approximation such interaction as there is must be due to Coulomb forces only, and must be independent of the ionic type. This is clearly only approximately true since the partial enthalpy changes show that there is a small interaction dependent on composition, but it is sufficiently
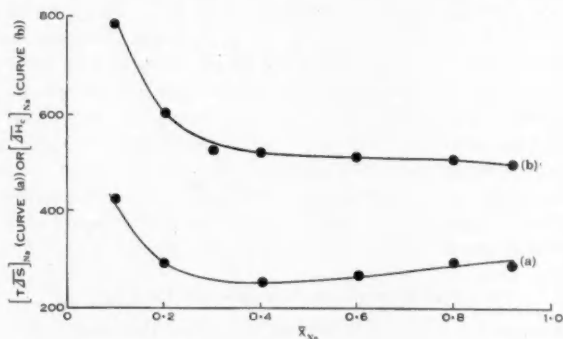

Fig. 6.—Curve (a) $T[\overline{\triangle S_c}]_{Na}$ and curve (b) $[\overline{\triangle H_c}]_{Na}$ plotted as functions of $\overline{X}_{Na}$.

small for the entropy changes to be practically ideal. We might expect therefore that the partial heats $\overline{\triangle H}_{Na}$ and $\overline{\triangle H}_{H}$ (which would be constant if there were no ionic interaction) would be to a first approximation linear with $\overline{X}_{Na}$. It will be seen from Figure 3 that this is so, except when $\overline{X}_{Na}$ is low (see Table 1).

Now, in gaseous sorption, Everett (1950) has shown that, if the excess entropy of a system forming a localized monolayer in the adsorber phase is plotted against the enthalpy, a straight line is obtained for a large number of adsorbates on gas charcoal, and this he suggests might very well be a general phenomenon, similar to the Barclay-Butler relation in liquids. In gaseous sorption the excess entropy is obtained by subtracting the term $-R \ln [\theta/(1-\theta)]$, where θ is the coverage, from the total entropy; in ion exchange the corresponding quantity is $-R \ln \overline{X}_{Na}/(1-\overline{X}_{Na})$. In other words, the entropy plotted in Figure 7 is in fact the excess entropy. A priori, one would expect a straight line to be obtained only for ion-exchange pairs in which the interaction forces are similar in type and different only in magnitude. Although with different exchangers, the three sets of results plotted in Figure 7 are of this type and give

quite a reasonable straight line. The barium-hydrogen system (in which the interactions must be of quite a different type) falls well off the line (see Section V).
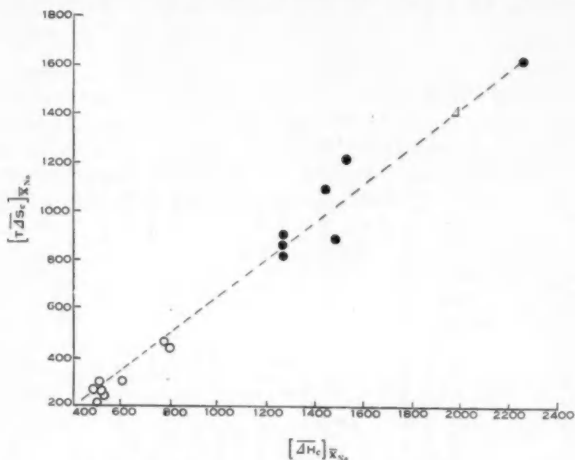

Fig. 7.—$[\overline{\triangle S_c}]_{\overline{X}_{Na}}$ plotted as a function of $[\triangle H_c]_{\overline{X}_{Na}}$.

○ Sodium-hydrogen exchange (Duncan and Lister 1949*a*).
● Potassium-hydrogen exchange (Cosgrove and Strickland 1950).
△ Potassium-hydrogen exchange (Kressman and Kitchener 1949).

V. EVALUATION OF PARTIAL THERMODYNAMIC QUANTITIES FOR THE BARIUM-HYDROGEN SYSTEM

(a) *Calculated and Experimental Mass Products*

In replacing the hydrogen of an exchanger by barium ions there is considerable contraction of the resin. Assuming that the effective charge of the resin structure is unity (Glueckauf 1952), the ionic strength increases from $6 \cdot 13$ to $13 \cdot 18$. Over this range $\overline{\gamma}_H^0$ increases from $1 \cdot 25$ to 390 (Duncan 1952) and $\overline{\gamma}_{Ba}^0$ from $0 \cdot 009$ to $0 \cdot 23$ (calculated from osmotic data (Glueckauf and Kitt, personal communication)), the absolute value of $\overline{\gamma}_{Ba}^0$ being fixed at $0 \cdot 227$ for $I = 13 \cdot 7$ by application of the Gibbs-Duhem equation to the exchange isotherm (Duncan and Lister 1949*b*; Duncan, forthcoming publication). We should therefore expect the mass-product to increase steeply with increasing $\overline{X}_{Ba}$. In fact, however, it was found to decrease somewhat as $\overline{X}_{Ba}$ tended to unity after passing through a maximum (Duncan and Lister 1949*b*). Thus, theory is quite inadequate in explaining the shape of the isotherm in this case. This is because of ionic interaction, the nature of which can be ascertained by considering the partial thermodynamic quantities calculated from equilibrium data (Table 2).

(b) *The Partial Molal Enthalpies (Fig. 8)*

It will be noticed that $\overline{\Delta H}_{Ba}$ is highly negative, but unlike $\overline{\Delta H}_{Na}$ (Fig. 2) it becomes more negative as the exchanger becomes denuded of hydrogen ions.

TABLE 2

EVALUATION OF THERMODYNAMIC FUNCTIONS FROM EXPERIMENTAL DATA FOR Ba/H EXCHANGE

The absolute accuracy is indicated by the number of significant figures, except for $\Delta \bar{G}_H$ and $\Delta \bar{H}_H$, for which the figures indicate only relative values and the absolute accuracy is only ± 1 and ± 10 per cent. respectively

$\bar{X}_{Ba}$	$(X_{Ba})_{80}$	$(X_{Ba})_{57}$	$\{BaCl_2\}$	$\Delta \bar{G}_{Ba} = 3RT$ $\times \ln[\{BaCl_2\}(\gamma^{\pm}|BaCl_2]$	$\Delta \bar{H}_{Ba}$	$(T\Delta S)_{Ba}$	$\{HCl\}$	$\Delta \bar{G}_H = 2RT$ $\times \ln[\{HCl\}](\gamma^{\pm}|HCl]$	$\Delta \bar{H}_H$	$(T\Delta S)_H$
0·1	0·000314	0·000408	0·0000157	−20,000	2530	17500	0·154	−2260	1·2	2260
0·2	0·000626	0·000860	0·0000313	−18,730	3030	15700	0·154	−2260	1·4	2260
0·3	0·00106	0·00150	0·000053	−17,800	3310	14500	0·154	−2260	1·8	2260
0·4	0·00192	0·00273	0·000096	−16,750	3370	13400	0·153	−2262	3·3	2265
0·5	0·00363	0·00528	0·000181	−15,680	3550	12100	0·153	−2262	10·4	2270
0·6	0·00686	0·0118	0·000343	−14,420	5160	9260	0·153	−2262	32·3	2295
0·7	0·0123	0·0300	0·000615	−13,330	8510	4820	0·151	−2228	111·6	2340
0·8	0·0400	0·0830	0·00200	−11,220	6960	4260	0·147	−2310	344·4	2655

This implies that the barium ions become more ion-paired, as might be expected when it is remembered that on account of (i) the decrease in volume of the exchanger and (ii) the replacement of a singly charged by a doubly charged cation, the ionic strength practically doubles.

The behaviour of $\overline{\Delta H}_H$ in the sodium-hydrogen and the barium-hydrogen system is similar, but the absolute values are considerably lower in the latter case. This means that the hydrogen ion is in much the same ionic state as in the external solution, presumably because the barium ion requires practically no hydration water and, as will be seen in Section V(c), interacts more with the sulphonic acid groups than with the hydrogen ions.
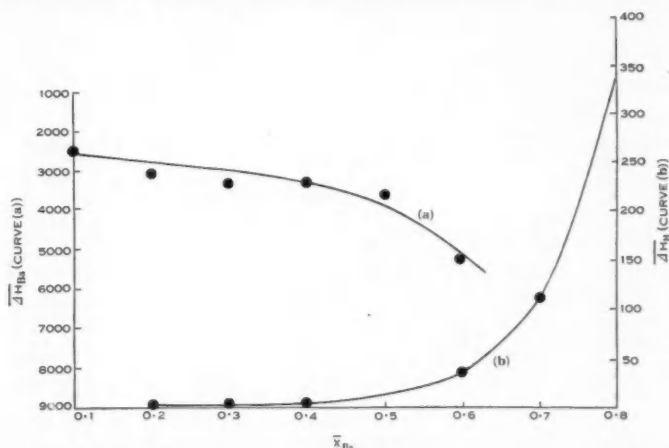

Fig. 8.—Partial molal heats of barium chloride and hydrochloric acid in the barium-hydrogen exchange reaction on " Dowex 50 ".

(a) Barium (negative).   (b) Hydrogen (positive).

The value of $\overline{\Delta H}_H$ in a nearly completely hydrogen-saturated exchanger should be the same no matter what the nature of the other cation since the differences of ionic interaction becomes negligible. By extrapolating the plots of $\overline{\Delta H}_H$ for these two systems* to $\overline{X}_H = 1$ we obtain $\overline{\Delta H}_H$ practically equal to zero in both cases. This confirms the similarity of ionic state of the hydrogen ion in near-hydrogen-saturated exchangers and in the external solution. It

* The experimental results in the Na/H exchange reaction were determined with an early sample of exchanger which gave sharply decreasing values of K_c below $\overline{X}_{Na} = 0 \cdot 1$. Above $\overline{X}_{Na} = 0 \cdot 2$, the trend was normal (Duncan and Lister 1949a). Later samples did not show this defect (see Fig. 1), which feature we ascribed to inhomogeneities in the cross-linking of the resin. The values of $\overline{\Delta H}_{Na}$ below $\overline{X}_{Na} = 0 \cdot 2$ in Figure 3 are therefore omitted, as they are believed to be associated with this feature. The corresponding values of $\overline{\Delta H}_H$ and $\overline{\Delta S}_H$ would not of course be expected to show any deviations as the resin is nearly hydrogen saturated ; nor does $\overline{\Delta S}_{Na}$ seem to be anomalous either.

also affords confirmation of our earlier conclusion (Duncan 1952) from salt uptake and osmotic data that the hydrogen ion in an ion exchanger is practically completely ionized.

Finally, since $\overline{\Delta H}_H$ does not vary widely over the greater part of the Ba/H isotherm, we may conclude that any interaction in which the hydrogen takes part must be practically constant. On the other hand, since the values of $\overline{\Delta H}_{Ba}$ are quite high, there must be quite substantial interaction between the barium ion and the resinate structure. This is confirmed by (i) the fact that the barium resinate has a rather lower conductivity than would be expected from solutions of barium salts at comparable concentrations (Heymann and O'Donnell 1949) and (ii) the partial entropy values for the barium ion (see next section).
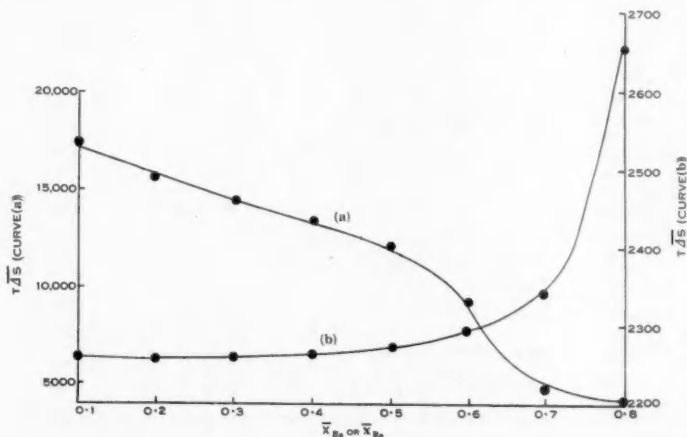

Fig. 9.—Partial molal entropies of barium chloride and hydrochloric acid in the barium-hydrogen exchange reaction on " Dowex 50 ".

(a) Barium.   (b) Hydrogen.

(c) The Partial Entropies

These (shown in Fig. 9) are by no means straight lines. The theoretical slope may be calculated by differentiation of the equation analogous to equation (8), namely,

$$\bar{S}^c = R \ln \left\{ \frac{[\frac{1}{2}(2N_{Ba}+N_H)]!}{N_{Ba}!\,(\frac{1}{2}N_H)!} \right\}, \qquad \dots\dots\dots (13)$$

where N_{Ba} and N_H are the number of moles of the two ions. Hence it can be shown that

$$\overline{\Delta S}_H^c = -\frac{R}{2} \ln \left(\frac{N_H}{2N_{Ba}} \right) = -\frac{R}{2} \ln \left[\frac{\overline{\overline{X}}_H}{1-\overline{\overline{X}}_H} \right], \qquad \dots\dots (14)$$

and

$$\overline{\Delta S}_{\text{Ba}}^{c} = -R \ln\left(\frac{2N_{\text{Ba}}}{N_{\text{H}}}\right) = -R \ln\left\{\frac{\overline{X}_{\text{Ba}}}{1-\overline{X}_{\text{Ba}}}\right\}. \quad \ldots\ldots \quad (15)$$

The lines corresponding to these slopes are shown in Figure 10. They have respectively slopes of RT and $3RT$ for the hydrogen and barium resinates, the factors of 2 and 3 respectively arising because contributions from the mono-valent anions were included in the calculated free energies.

It will be seen from Figure 10 that in both cases the entropy plots only approximate to the theoretical slope when the ions are present in small amounts. This could arise at high barium-ion concentrations merely from the approximate
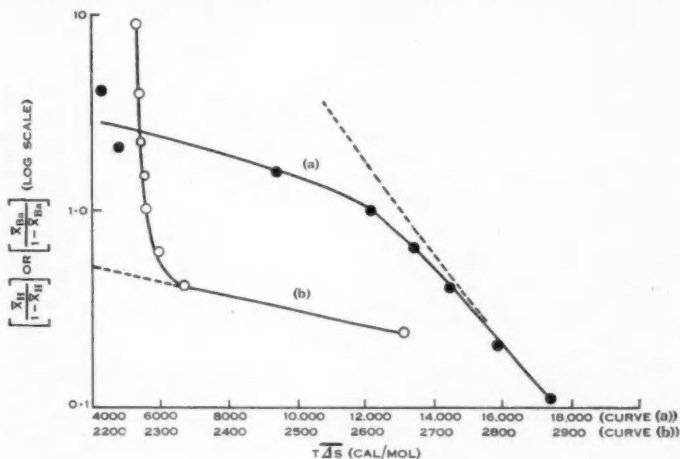

Fig. 10.—Variation of partial molal entropies of barium-hydrogen exchange reaction with resin composition.

(a) Barium.   (b) Hydrogen.   The lines are drawn with the theoretical slope.

nature of equation (13), which does not take into account the impossibility of a barium ion being fixed on two separated sites. But it cannot explain the hydrogen curve, which is most nearly of the theoretical slope just in the region where such an objection would obtain. Further, deviations at small values of $\overline{X}_{\text{Ba}}$ are most unlikely to be due to such a cause, as it is in this region that equation (15) would be valid. On the other hand, such deviations would be expected even if equation (15) were exact, since the heat data for the barium ion show that there are considerable interaction forces. A fall in entropy with increasing $\overline{X}_{\text{Ba}}$ would also be in agreement with the earlier conclusion that this interaction is predominantly anion-cation in type since the energies of the adsorption sites would be modified as the barium ions are introduced into the

exchanger. From the shape of the entropy plot for the hydrogen ion it is clear that this occurs.

If we now calculate the mean molar entropies and heats, namely,

$$T\overline{\Delta S}_M = T\bar{x}_{Ba}\overline{\Delta S}_{Ba} + T(\bar{X}_H)\overline{\Delta S}_H,$$

and

$$\overline{\Delta H}_M = \bar{x}_{Ba}\overline{\Delta H}_{Ba} + \bar{X}_H\overline{\Delta H}_H,$$

where $\bar{x}_{Ba}$ is the number of moles barium ion/equivalent of exchanger and $\bar{X}_H$ is the number of moles or equivalents of hydrogen ion/equivalent of exchanger, curves such as shown in Figure 11 are obtained. In this figure the abscissa
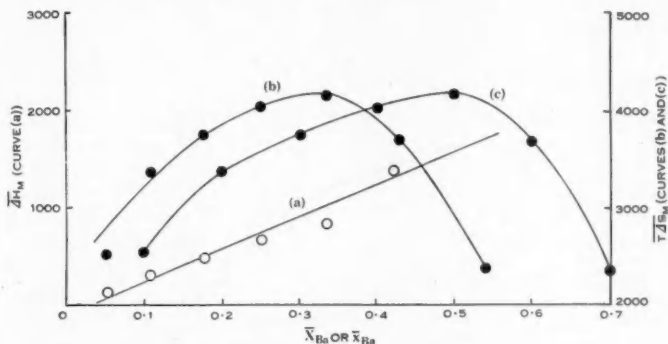

Fig. 11.—Mean molal entropy and heat for barium-hydrogen exchange.
  (a) $\overline{\Delta H}_M$ as a function of $\bar{X}_{Ba}$.
  (b) $T\overline{\Delta S}_M$ as a function of $\bar{X}_{Ba}$.
  (c) $T\overline{\Delta S}_M$ as a function of $\bar{x}_{Ba}$.

is the molar fraction of the barium ion, $N_{Ba}/(N_{Ba}+N_H)$, where N is the number of moles of the appropriate species. It will be seen that the mean molal heat is almost linear with molar fraction, as would be expected if there were relatively little interaction between the two cations. On the other hand, the mean molal entropies are by no means symmetrical about the equimolar point, although it will be seen from Figure 11 that it is reasonably symmetrical with respect to the point where the number of equivalents of the two ions is the same. It would appear therefore that the fundamental quantity determining the statistical effects of ion exchange is the number of fixed anion groups per mole. This conclusion might have been expected, but it is worth emphasizing since some authors regard the number of ions as the significant quantity. On the other hand, it is evident that it is the number of ions which determines the enthalpy terms involved (whether these arise from anion-cation, or cation-cation inter-action) and that these are remarkably little affected by the number of fixed anion groups.

(d) Experimentally Evaluated Free Energies, Heats, and Entropies

The experimentally determined mass-product for the barium-hydrogen system

$$K_c = \frac{[\overline{\text{Ba}}]}{[\overline{\text{H}}]^2} \times \frac{\{\text{H}\}^2}{\{\text{Ba}\}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (16)$$

may be written (Duncan and Lister 1949a, 1949b) in the form

$$K_c = \frac{\overline{X}_{\text{Ba}}}{(1 - \overline{X}_{\text{Ba}})^2} \times \frac{w}{\overline{C}} \times \frac{\{\text{HCl}\}^2}{\{\text{BaCl}_2\}}, \quad \ldots\ldots\ldots\ldots \quad (17)$$

where w is the water content of the exchanger in ml/g hydrogen resin, and $\overline{C}$ is the capacity in m-equiv/g hydrogen exchanger.
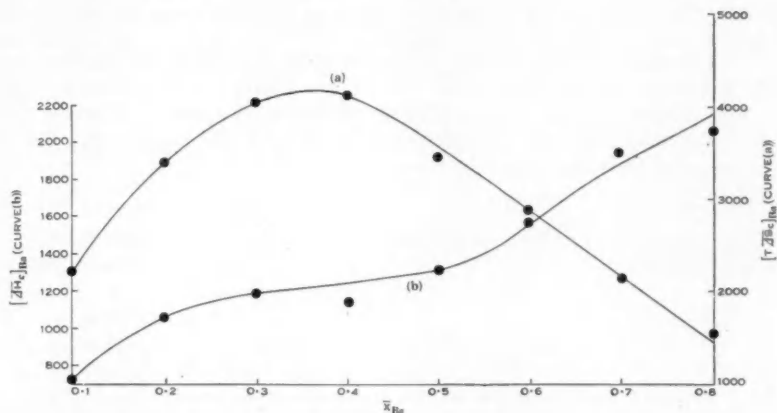

Fig. 12.—$T[\overline{\Delta S}_c]_{\text{Ba}}$ (curve (a)) and $[\overline{\Delta H}_c]_{\text{Ba}}$ (curve (b)) plotted as functions of $\overline{X}_{\text{Ba}}$.

Following Section IV it can then be shown that

$$[\overline{\Delta S}_c]_{\overline{X}_{\text{Ba}}} = -\left[\frac{\partial(\overline{\Delta G}_c)}{\partial T}\right]_{\overline{X}_{\text{Ba}}} = -\left[\frac{\partial w}{\partial T}\right]_{\overline{X}_{\text{Ba}}}. \quad \ldots\ldots \quad (18)$$

Thus, provided there is no change in the water content with temperature, for a given value of $\overline{X}_{\text{Ba}}$, the configurational entropy should be zero. The water content of an exchanger is undoubtedly temperature dependent. With a hydrogen-saturated sulphonated polystyrene (10 per cent. D.V.B.) in equilibrium with water the concentration was observed to fall from 6·8 at 25 °C to 5·9 at 0 °C (Glueckauf and Kitt, personal communication). But in the present case the variable water-content contributes not more than 0·03 cal/mol deg⁻¹ to the values of the entropies of exchange, which is insignificant. When the entropies of Figure 12 are compared with those of Figure 6, for uni-univalent systems it will be seen that the configurational entropy is very high for quite

moderate heat terms. Hence the Ba/H system must be fundamentally different in type from the Na/H and K/H exchange reactions, as had been concluded earlier.

VI. Effect of Volume Changes on Thermodynamic Quantities

Since volume changes are known to be large in some cases and the above equations are valid only when there is no volume change, it must now be shown that the above conclusions will not be significantly affected by neglect of these factors.

The partial thermodynamic quantities have been evaluated in order to assess the behaviour of the individual ions in the exchanger. We are not so much interested in the activity a_j of the species j in the external solution as in the activity $\bar{a}_j$ of that species in an unstrained exchanger of the same composition. These two quantities are related by the equation

$$\overline{\Delta G}_j = RT \ln a_j = RT \ln \bar{a}_j + Pv_j, \qquad \ldots \ldots \ldots \ldots \textbf{(19)}$$

where P is the " swelling pressure ", v_j is the molar volume of the species j, and $\overline{\Delta G}_j$ is the free energy excess over that of the species j in the standard state (infinite dilution in pure water). If P were constant, changes in $\overline{\Delta G}_j$ would then accurately reflect the changes in activity occurring in the exchanger. If P is not constant, then we must add a correction factor

$$\Delta G_A = Pv_j, \qquad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \textbf{(20)}$$

together with the corresponding heats and entropies

$$\overline{\Delta H}_A = -v_j T \left[\frac{\partial P}{\partial T}\right]_x + Pv_j, \qquad \ldots \ldots \ldots \ldots \ldots \textbf{(21)}$$

and

$$\Delta S_A = -\frac{\partial(\overline{\Delta G}_A)}{\partial T} = -v_j \left[\frac{\partial P}{\partial T}\right]_x, \qquad \ldots \ldots \ldots \ldots \textbf{(22)}$$

where v_j is assumed to be temperature independent. In the case of the sodium-hydrogen system, the effect of the term $\overline{\Delta G}_A$ in the calculations is quite negligible. Even for the barium-hydrogen system, the error is not large. Thus Table 3 shows the error in the assessment of the partial thermodynamic functions for

Table 3	
	Hydrogen Saturated Exchanger
P (for resinate) ..	280 atm
v_j (chloride)*	20 ml/mol
$\left[\dfrac{\partial P}{\partial T}\right]$ (for resinate) ..	1·52 atm/°C
ΔG_A	181 cal/mol
ΔH_A	169 cal/mol
ΔS_A	12 cal/mol

* Harned and Owen (1950).

the hydrogen ion, calculated from results of Glueckauf and Kitt (personal communication). The corresponding values for the barium ion would be of comparable magnitude. The shapes of the curves of Section V (Figs. 8–12) would not therefore be seriously affected.

VII. Conclusions

It will be seen that an examination of the temperature variation of the exchange reaction leads to information about the behaviour of cations in an ion exchanger quite distinct from the behaviour of the associated anions. The treatment shows that the sodium and hydrogen ions at concentrations of 6–10 molar are completely mobile and similar in ionic state to those existing in solution. The interaction between the two cations and between cations and anion is small, to a first approximation linear, and does not greatly alter the behaviour of either. On the other hand, interaction between barium ions and the resinate structure seems to be so strong that the barium cannot be regarded as a normal ion, such as might exist in dilute aqueous solutions. The hydrogen ion, however, is still completely ionized and freely mobile.

VIII. Symbols

In this paper the following symbols have been used :

$\overline{C}$, capacity of exchanger (m-equiv/g),

G, Gibbs free energy,

H, enthalpy,

K_c, mass law product allowing for the activity coefficients of the electrolytes
    in the aqueous solution,

I, ionic strength,

N, number of adsorption sites in an ion exchanger,

p, pressure of a gas,

P, energy change per unit volume (has the dimensions of pressure),

S, entropy,

v, molar volume,

w, weight of water taken up by an exchanger,

x, ionic molar fraction,

X, ionic equivalent fraction,

γ, mean molal ionic activity coefficient,

$\{\ \}$, thermodynamic activity,

$[\ ]$, molal concentration (mol/1000 g water).

A bar as in $\overline{H}$ or $\overline{\gamma}$ denotes that the quantity refers to the exchanger phase.

A heavy bar as in $\overline{\Delta S}$ denotes that the quantity is the partial thermodynamic
    function of the species in the appropriate phase.

No difference mark as in $[H]$ or γ_H denotes that the quantity refers to the
    external solution.

Suffix T as in $\overline{\Delta S}_T$ refers to both ions in the exchanger phase only.

Suffix 20, as in $NaCl_{20}$, refers to the temperature (20 °C).

Suffix c, as in $\overline{\Delta H}_c$, indicates that the quantity is derived from the mass-
    product K_c.

Suffix j, as in $\bar{a}_j$, refers to the component j.

Suffix A, as in $\overline{\Delta G}_A$, indicates that the quantity is a correction factor added to take account of resin swelling.

Superscript c, as in $\overline{\Delta S^c}$, refers to the configurational entropy calculated from statistical mechanics.

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THE BEHAVIOUR OF FLUIDS OF QUASI–SPHERICAL MOLECULES

IV. CONCERNING TROUTON'S AND HILDEBRAND'S RULES

By S. D. HAMANN*

Summary

An examination of the theoretical foundations of Trouton's and Hildebrand's rules gives an explanation of the greater generality of Hildebrand's rule. In a group of liquids obeying the principle of corresponding states those with the larger critical volumes V_c have smaller Hildebrand entropies of evaporation. But in many groups of non-polar liquids an increase in V_c is accompanied by a change in the form of the molecular interaction potential (with consequent departure from the principle of corresponding states) and this change can produce a compensating increase in Hildebrand's entropy.

I. INTRODUCTION

Pictet (1876) and Trouton (1884) pointed out that the molar heat of evaporation $\Delta_e H$ of a liquid is roughly proportional to its normal boiling temperature T_b on the absolute scale. By this rule the molar entropy of evaporation at 1 atm,

$$\Delta_e S = \left(\frac{\Delta_e H}{T_b} \right)_{p=1},$$

should be almost the same for all liquids. Actually it varies by as much as 20 per cent. even within a homologous group of non-polar liquids such as the normal paraffin hydrocarbons. Hildebrand (1915) showed that greater constancy is found in the entropy of evaporation of liquids, not at their normal boiling points, but at temperatures such that their vapours have equal molar volumes.

Neither the Pictet-Trouton rule nor Hildebrand's rule is in accordance with the principle of corresponding states, which requires the molar entropies of evaporation of liquids to be equal at the same *reduced* temperature, vapour pressure, or volume. In a group of liquids conforming to the principle of corresponding states the Pictet-Trouton entropy would vary with critical pressure, and Hildebrand's entropy with critical volume. Surprisingly it often

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happens that Hildebrand's rule applies quite well to liquids of widely different critical volumes.

The purpose of this paper is to examine a possible reason for the success of Hildebrand's relation in these cases.

II. Theory of Trouton's and Hildebrand's Rules

Lennard-Jones and Devonshire (1938) have considered the theoretical implications of Trouton's and Hildebrand's rules in a general manner. Their method will be used here to derive some numerical relations between the entropies of evaporation and the critical constants. The cell model of Lennard-Jones and Devonshire (1937) gives the vapour pressure p' of a liquid in the approximate form

$$\log_e \frac{p'}{zp_0} = A - B\frac{zT_0}{T}, \quad \ldots\ldots\ldots\ldots (1)$$

where A and B are constants for a particular type of molecular interaction potential, p_0 and T_0 are characteristic pressures and temperatures defined in Part II of this series (Hamann and Lambert 1954b), and z is the number of nearest-neighbour molecules in the liquid lattice. From the approximate thermodynamic relation

$$\Delta_e H = RT^2 \frac{\mathrm{d} \log_e p'}{\mathrm{d}T}, \quad \ldots\ldots\ldots\ldots (2)$$

the entropy of evaporation at the temperature T is

$$\frac{\Delta_e S}{R} = \frac{\Delta_e H}{RT} = \frac{BzT_0}{T}. \quad \ldots\ldots\ldots\ldots (3)$$

(a) Trouton's Rule

Introducing the critical pressure p_c and the relation (3), (1) can be written

$$\log_e \frac{p'}{p_c} \cdot \frac{p_c}{zp_0} = A - \frac{\Delta_e S}{R}, \quad \ldots\ldots\ldots\ldots (4)$$

so that the Trouton entropy of evaporation, $(\Delta_e S)_{\mathrm{Tn}}$ at $p' = 1$ atm, is

$$\frac{(\Delta_e S)_{\mathrm{Tn}}}{R} = A - \log_e \frac{p_c}{zp_0} + \log_e (p_c/\mathrm{atm}). \quad \ldots\ldots\ldots (5)$$

The quantities A and p_c/zp_0 were worked out in Part II of this series (Hamann and Lambert 1954b) for liquids whose molecules interact according to (12,6) and (28,7) bireciprocal potentials. They are

Potential	A	p_c/zp_0
(12,6)	2·172*	0·0392
(28,7)	3·698*	0·0191

* These values are based on the approximation: $V_L/V_0 = 1$ (see Hamann and Lambert 1954b).

The theoretical Trouton entropies for the two potentials are thus

Potential

$$(12,6): \quad \frac{(\Delta_e S)_{\mathrm{Tn}}}{R} = 5 \cdot 411 + \log_e \ (p_c/\mathrm{atm}), \quad \dots\dots\dots \ (6)$$

$$(28,7): \quad \frac{(\Delta_e S)_{\mathrm{Tn}}}{R} = 7 \cdot 656 + \log_e \ (p_c/\mathrm{atm}). \quad \dots\dots\dots \ (7)$$

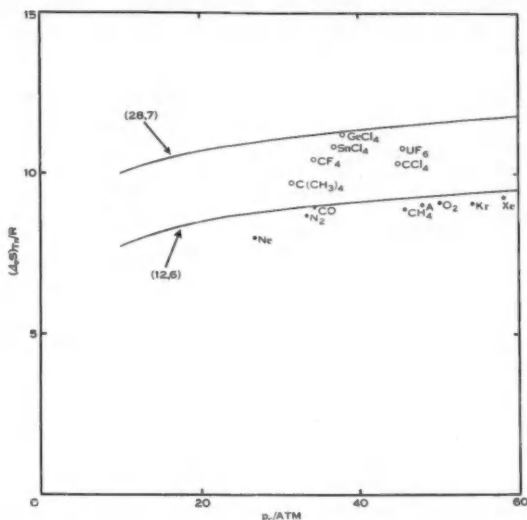They have been plotted against p_c in Figure 1.

Fig. 1.—Theoretical and experimental Trouton entropies.

(b) Hildebrand's Rule

If the vapour can be considered an ideal gas then

$$p' = kT/V', \quad \dots\dots\dots\dots\dots\dots\dots \ (8)$$

where V' is the volume per molecule of the vapour phase and k is Boltzmann's constant. Also

$$p_0 = kT_0/V_0,$$

where V_0 is a characteristic volume defined in Part II of this series (Hamann and Lambert 1954b).   Equation (1) can then be written in terms of the critical volume V_c

$$\log_e \left[\left(\frac{V_c}{V'} \right) \left(\frac{V_0}{V_c} \right) \left(\frac{T}{zT_0} \right) \right] = A - \frac{BzT_0}{T}, \quad \dots\dots\dots \ (9)$$

and so, from (3),

$$\log_e \frac{V_c}{V'} = \log_e \frac{V_c}{V_0} + \log_e \frac{\Delta_e S}{R} - \log_e B + A - \frac{\Delta_e S}{R}. \quad \dots \ (10)$$

Following Hildebrand we take V' to be 10 l/g-mol. A, B, and V_c/V_0 were calculated in Part II of this series; they are listed below.

Potential	A	B	V_c/V_0
(12,6)	2·172*	0·692*	2
(28,7)	3·698*	0·562*	2·5

The Hildebrand entropies are then given by the relations:

Potential

$$(12,6): \quad \frac{(\Delta_e S)_{\text{Hd}}}{R} - \log_e \frac{(\Delta_e S)_{\text{Hd}}}{R} = 12\cdot443 - \log_e (V_c/\text{cm}^3\,\text{g-mol}^{-1}),$$

$$\dots\dots\dots\dots \textbf{(11)}$$

$$(28,7): \quad \frac{(\Delta_e S)_{\text{Hd}}}{R} - \log_e \frac{(\Delta_e S)_{\text{Hd}}}{R} = 14\cdot400 - \log_e (V_c/\text{cm}^3\,\text{g-mol}^{-1}),$$

$$\dots\dots\dots\dots \textbf{(12)}$$

$(\Delta_e S)_{\text{Hd}}/R$ is plotted against V_c in Figure 2.
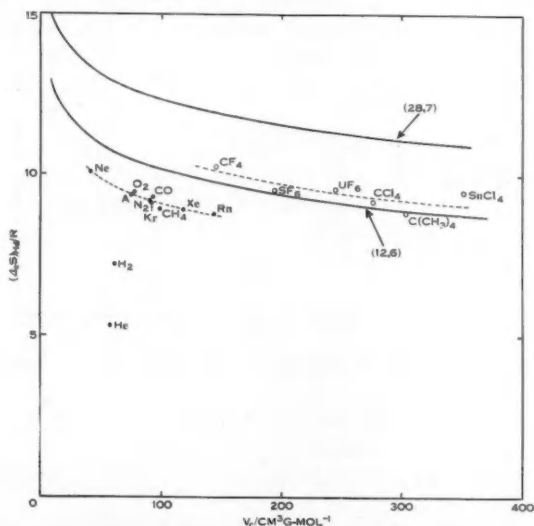
Fig. 2.—Theoretical and experimental Hildebrand entropies. The anomalous behaviour of hydrogen and helium arises from quantization of the motion of their molecules in the liquid phase.

III. DISCUSSION

The figures show that the theoretical values of $(\Delta_e S)_{\text{Tn}}/R$ and $(\Delta_e S)_{\text{Hd}}/R$ vary considerably with p_c and V_c. Furthermore these changes appear in the experimental entropies of evaporation of groups of liquids which obey the

* These values are based on the approximation: $V_L/V_0 = 1$ (see Hamann and Lambert 1954b).

principle of corresponding states (e.g. the condensed inert gases). Hildebrand's entropy for these liquids varies just as much as Trouton's entropy. It is quite wrong to suppose that it is because " the critical volume is more nearly constant for a wide range of non-polar substances than is the critical pressure " (Hildebrand and Scott 1950), that Hildebrand's rule is sometimes an improvement upon Trouton's rule. But the success of Hildebrand's rule *can* arise from a compensating change in the form of the intermolecular potential which may accompany the change in critical volume.

The earlier papers in this series (Hamann and Lambert 1954a, 1954b) showed that whilst the interaction potential of the inert gas molecules is well described by a (12,6) bireciprocal formula in the intermolecular separation, that of polyatomic quasi-spherical molecules like CCl_4 is better represented by a (28,7) potential. Equations (**11**) and (**12**) and Figure 2 show that this change of potential would increase Hildebrand's entropy if V_c were unchanged. However, the quasi-spherical molecules are nearly always larger than the inert gas molecules and V_c is correspondingly greater. This increase in V_c reduces the entropy of evaporation and largely compensates for the change in potential. Figures 1 and 2 show that a similar compensation does not occur in Trouton's entropies because, contrary to the statement of Hildebrand and Scott quoted above, the critical pressures vary less than the critical volumes.

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SOLVENT EFFECTS IN INFRA-RED SPECTRA: C=O, C-H, AND C-C VIBRATIONS*

By N. S. Bayliss,† A. R. H. Cole,†‡ and L. H. Little†§

Summary

Frequency displacements and intensities are reported for the C=O stretching fundamental and first overtone in acetone, acetaldehyde, and di*iso*propyl ketone, for the chloroform C—H stretching fundamental, and for the acetonitrile C—C stretching fundamental, all in a variety of non-polar and polar solvents. The solvent displacement of C—C is very small ($\sim$1 K), for C—H and C=O it is to the red and of the order of 10–20 K, with C=O overtones being displaced about twice as much as the fundamentals. The Kirkwood relation between the frequency displacement and solvent dielectric constant is inadequate if the static D is used. The C=O results can be interpreted in terms of two superimposed effects: (i) the electronic polarization of the solvent causes a frequency shift related to the solvent refractive index, and (ii) in polar solvents there is an additional shift due to solvent dipole orientation. Effect (ii) causes an added contribution to the intensity. The C—H results do not fit easily into this interpretation.

I. Introduction

Systematic studies of solvent effects on infra-red vibration spectra are not very numerous in relation to the whole infra-red literature, and the phenomena are still far from being completely described either experimentally or theoretically. In particular there has been less attention paid to intensity changes than to frequency shifts. In this paper we describe studies of the C=O stretching frequency, both the fundamental and overtone bands, in several simple carbonyl compounds, of the C—H stretching frequency in chloroform, and of the C—C stretching frequency of acetonitrile, all in a variety of solvents chosen to cover as wide a range of dielectric constant, refractive index, and polarity as was

experimentally convenient. Frequency shifts and changes in band shape and intensity have been measured as carefully as possible.

In the belief that before the totality of solvent effects on spectra can be understood, the purely physical effects (which are always present whether or not they are accompanied by chemical or quasi-chemical solute-solvent interaction) must be investigated, we have restricted the present study to cases where the solvent effect should be mainly physical in nature. Thus Hartwell, Richards, and Thompson (1948), who have surveyed solvent effects on a variety of carbonyl compounds, have shown that hydrogen bonding is probably not significant in simple ketone $C=O$ frequencies, but that it may well be important in the $C=O$ frequencies of acids and amides.

II. EXPERIMENTAL

All the substances used were carefully purified, and the physical constants obtained for the solutes were as follows ; the values in parentheses being from Timmermans (1950) or in the case of di*iso*propyl ketone, from Beilstein (1941) :

Acetone : b.p. $46 \pm 0 \cdot 5$ °C $(46 \cdot 3$ °C$)$; n_D^{15} $1 \cdot 3616$ $(1 \cdot 3616)$; d_4^{25} $0 \cdot 7844$ $(0 \cdot 7846)$.

Di*iso*propyl ketone : b.p. 124–$124 \cdot 5$ °C $(123$–125 °C$)$; n_D^{18} $1 \cdot 4010$ $(n_D^{20}$ $1 \cdot 4007)$; d_4^{25} $0 \cdot 80016$ $(d_4^{20}$ $0 \cdot 8062$–$0 \cdot 8087)$.

Acetaldehyde : prepared from sulphuric acid and paraldehyde and re-fractionated ; physical constants not determined.

Chloroform : b.p. $61 \pm 0 \cdot 5$ °C $(61 \cdot 2$ °C$)$; n_D^{15} $1 \cdot 4486$ $(1 \cdot 4486)$; d_4^{25} $1 \cdot 4795$ $(1 \cdot 4797)$.

Acetonitrile : b.p. $82 \pm 0 \cdot 5$ °C $(81 \cdot 6$ °C$)$; n_D^{18} $1 \cdot 3450$ $(1 \cdot 3447)$; d_4^{25} $0 \cdot 7767$ $(0 \cdot 7768)$.

The physical constants for the solvents were also in good agreement with the literature values (Timmermans 1950).

TABLE 1
EXPERIMENTAL DETAILS

Vibration	Optical System	Calibration Data	Effective Slit-Width (K)
$C=O$ fundamental	Calcium fluoride single-pass	Water vapour (Nielsen 1941)	3
$C=O$ first overtone	Calcium fluoride single-pass	Ammonia (Dennison and Hardy 1932)	8
C—H stretching (chloroform)	Calcium fluoride double-pass (Rochester and Martin 1951 ; Walsh 1951)	Methane (Nielsen and Nielsen 1935) Hydrogen chloride (Meyer and Levin 1929)	5
C—C stretching (acetonitrile)	Sodium chloride double-pass	Ammonia (Oetjen, Kao, and Randall 1942)	$2 \cdot 5$

The infra-red spectrometer is a Grubb Parsons Model S3A, with Perkin-Elmer chopper and rectifier assembly, thermocouple and amplifier, and with a Brown " Electronik " recorder.   Table 1 shows the optical systems used, the effective slit-widths, and the calibration data.

The gas spectra used for frequency calibrations were recorded on each chart. The liquid cells varied in path length between $0 \cdot 1$ and 3 mm, the cell length being found in each case by focusing a microscope in turn on the inner faces of the sodium chloride windows.

TABLE 2
C=O FUNDAMENTAL—ACETONE

State	ν (K)	$\Delta\nu$ (K)	εmax.	$\Delta\nu_{\frac{1}{2}}$ (K)	Intensity
Vapour	1737·5	—	—	—	—
Solvents					
1. n-Hexane	1723·5	14	228	15	5570
2. $cyclo$Hexane	1723	14·5	257	13	5570
3. Carbon tetrachloride ..	1719	18·5	338	11·5	6960
4. Dioxan	1715·5	22	449	10	6800
5. Benzene	1717	20·5	404	10·5	6940
6. Tetrachloroethylene ..	1720	17·5	399	10·5	6950
7. Carbon disulphide	1717·5	20	327	12	5940
8. Diethyl ether	1721	16·5	337	11	6110
9. Chloroform	1711·5	26	445	13	8740
10. Bromoform	1708	29·5	493	12·5	9430
11. Ethylene dibromide ..	1713	24·5	457	11	8050
12. Pyridine	1713	24·5	443	10·5	7240
13. Acetone (liquid)	1714·5	23	—	—	—

The solutions were made up by weight in narrow necked flasks, a solvent evaporation correction being applied where necessary.   Ideal mixing was assumed in calculating the volume concentration in mole litre^{-1} required for the evaluation of extinction coefficients.   The concentrations were chosen to give between 50 and 70 per cent. absorption at the band maxima.

In order to determine each integrated band intensity, the apparent molar extinction coefficients (Ramsay 1952) were plotted against frequency in kaysers and the area under the curve found from Simpson's rule.   The integration was carried out to 40 K on either side of the maximum and wing corrections (amounting to about 10 per cent. of the area) were applied (Ramsay 1952). The apparent peak heights, half-widths, and integrated absorption intensities were corrected for finite slit-width (Ramsay 1952) but with the resolving power available in our spectrometer the intensity correction was usually less than 1 per cent.

The absorption bands measured were all overlapped to some extent by neighbouring bands.   In the cases of acetone and chloroform they were resolved graphically ; but this was not possible with acetonitrile or diisopropyl ketone

because of the uncertainty of the extent of the overlap. Acetone in most solvents showed two bands in the carbonyl region, a weak band at about 1750 K appearing beside the intense band near 1720 K (see Fig. 1). The intensity of the weak band was not reduced in experiments on acetone obtained from different sources and purified by different methods, and it must be concluded that it belongs to acetone itself, although its assignment is unknown.

The experimental results are recorded in Tables 2–7 where each solvent is identified with a serial number for easy comparison with the figures. The band frequencies ν, the displacements to lower frequency in solution $\Delta\nu$, and the band half-widths $\Delta\nu_{\frac{1}{2}}$ are all in kaysers (K); the maximum extinction coefficients $\varepsilon_{max.}$ are in mole^{-1} litre cm^{-1} from the usual relation $\log_{10}(I_0/I) = \varepsilon cl$, where I_0 and I are the incident and transmitted intensities, c is the concentration in

TABLE 3
C=O FUNDAMENTAL—DIISOPROPYL KETONE

State	ν (K)	$\Delta\nu$ (K)	$\varepsilon_{max.}$	$\Delta\nu_{\frac{1}{2}}$ (K)	Intensity
Vapour	1730	—	—	—	—
Solvents					
1. n-Hexane	1721·5	8·5	327	10	5840
2. cycloHexane	1720·5	9·5	342	10	5610
3. Carbon tetrachloride ..	1716·5	13·5	322	14	6430
4. Dioxan	1713	17	310	14·5	7310
5. Benzene	1714	16	316	15	6900
6. Tetrachloroethylene ..	1717·5	12·5	317	13·5	5970
7. Carbon disulphide ..	1715·5	14·5	320	13·5	6340
8. Diethyl ether	1718	12	286	13·5	5690
9. Chloroform	1707	23	263	19·5	7150
10. Bromoform	1704·5	25·5	316	19	8130
11. Ethylene dibromide ..	1709·5	20·5	288	17·5	7050
12. Pyridine	1709	21	316	16·5	7410
14. Diisopropyl ketone (liquid)..	1713·5	16·5	—	—	—

mole litre^{-1}, and l the path length in cm. The intensities are expressed as the areas $\int\varepsilon d\nu$ under the absorption curves, and are therefore in mole^{-1} litre cm^{-2}. Experimental conditions made it impossible to determine accurately the extinction coefficients and the integrated intensities for the C=O first overtones and for the C=O fundamental in acetaldehyde. The vapour fundamental bands (e.g. as in Fig. 1) all showed the P, Q, and R branches, and the recorded vapour frequencies are for the maximum of the Q branch in each case, since this can be located much more accurately than the band origin. Furthermore the band origins are impossible to locate in the solution spectra. The carbonyl overtone bands in the vapour were not completely resolved into branches and the frequencies were taken at the centre of the absorption.

The errors in the band frequencies do not exceed 0·5 K for the C=O fundamentals, 2 K for the C=O overtone, 1 K for C—H, and 0·5 K for C—C. Intensity measurements were reproducible to within ±5 per cent., and for comparison

it is noted that our value for the intensity of the acetone $C=O$ fundamental is within 5 per cent. of the value found by Barrow (1953).

Hartwell, Richards, and Thompson (1948) have recorded the acetone $C=O$ fundamental in a number of solvents; their frequencies are uniformly 4–6 K higher than ours. Owing to the internal calibration provided by the water-vapour bands on each of our charts, we consider that our frequencies are not subject to errors of this magnitude.

Intensity measurements were not carried out for acetaldehyde because of the uncertainty in the measurement of the concentration of its solutions.

III. Discussion

The solution phenomena can be discussed conveniently in terms of (a) the change in band envelope, (b) the frequency displacement, and (c) the change in intensity.
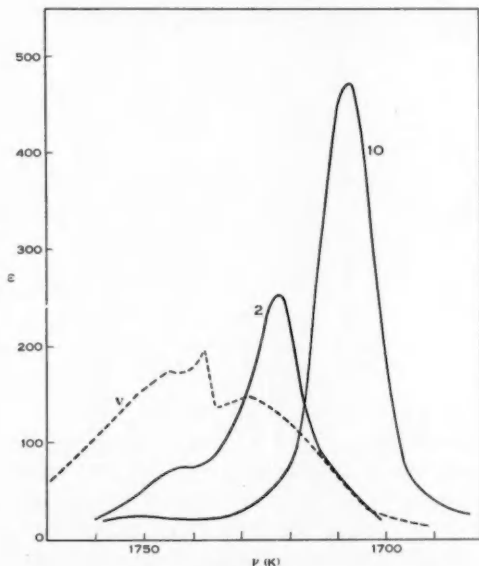
Fig. 1.—$C=O$ fundamental in the vapour (v), in cyclo-hexane (2), and in bromoform (10). Note resolved P, Q, and R branches in vapour; also the subsidiary band at about 1745 K in cyclohexane.

(a) The Change in Band Envelope

Figure 1, which is representative of our results, shows the envelope of the $C=O$ fundamental in acetone in the vapour state (on an arbitrary intensity scale) compared with the quantitative envelopes of the same band in two solvents. In keeping with the results of previous investigators on other solution bands (West and Edwards 1937; West 1939; Herzberg 1945; Richards and Burton 1949; Ramsay 1952) the characteristic P, Q, and R branches of the

vapour spectrum disappear in solution, and are replaced by a single, narrower band whose contour can be approximated by a Lorentz or by an error curve. There is no precise theory of this phenomenon ; but it is certainly due to the loss of free rotation by the solute molecule in solution, and its replacement by a thermal libration within the cage of solvent molecules. The half-width $\Delta\nu_{\frac{1}{2}}$ of each solution band varies from one solvent to another (Tables 2–7). In the case of the $C-Cl$ stretching frequency in chloroform, Whiffen (1953) found that $\Delta\nu_{\frac{1}{2}}$ increased with the polarity of the solvent ; but no such consistent behaviour can be discerned in our results. Thus while the half-width of the $C=O$ fundamental in di*iso*propyl ketone increases roughly with solvent polarity (Table 3), the reverse is true for the same band in acetone and acetaldehyde (Tables 2 and 4) where the greatest $\Delta\nu_{\frac{1}{2}}$ in each case is in the non-polar solvent hexane.

TABLE 4
$C=O$ FUNDAMENTAL—ACETALDEHYDE

State	ν (K)	$\Delta\nu$ (K)	$\Delta\nu_{\frac{1}{2}}$ (K)
Vapour	1746·5	—	—
Solvents			
1. *n*-Hexane	1736·5	10	24
2. *cyclo*Hexane..	1735·5	11	19·5
3. Carbon tetrachloride ..	1731·5	15	14
4. Dioxan	1726	20·5	9·5
5. Benzene	1727·5	19	12
6. Tetrachloroethylene ..	1731·5	15	12·5
7. Carbon disulphide	1729·5	17	14·5
8. Diethyl ether	1731	15·5	15
9. Chloroform	1725	21·5	11·5
10. Bromoform	—*	—	—
11. Ethylene dibromide ..	1724·5	22	10
12. Pyridine	1724	22·5	11

* Measurements could not be made in bromoform owing to chemical reaction.

(b) Frequency Displacements

In accordance with practically all previous experience in the infra-red (e.g. Herzberg 1945) the absorption frequencies are lowered in solution and in the liquid state. The $C=O$ first overtones are displaced about twice as much as the $C=O$ fundamentals ; the displacement of the $C-C$ fundamental in acetonitrile (Table 7), though definite, is very small possibly because as an " internal " vibration it is more protected from solvent influence than the more " exposed " $C=O$ and $C-H$ vibrations.

The theory of Kirkwood (see West and Edwards 1937) and of Bauer and Magat (1938) relates the frequency shift $\Delta\nu$ to the dielectric constant D of the solvent by

$$\frac{\Delta\nu}{\nu} = \frac{C(D-1)}{2D+1}, \quad \dots\dots\dots\dots\dots\dots (1)$$

where the factor C is complex and depends on the detail of the model used for the vibrating solute dipole. Quite apart from the value of C, equation (1) predicts that a plot of $\Delta\nu$ against the D function should be linear and pass through the origin, and this was found to be approximately true, for example, for HCl (West and Edwards 1937) and for O—H (Jones and Badger 1951). Warhurst (1949) found a correlation between $\Delta\nu$ and $\ln D$ for HCl, HF, and O—H. In Figure 2 we have plotted $\Delta\nu$ against the D function for the acetone C=O and the chloroform C—H fundamentals in the solvents whose properties are listed in Table 8. The other C=O fundamentals and the C=O overtones are omitted because their behaviour closely parallels that of the acetone C=O fundamental. Equation (1) is clearly inadequate, nor would there be an improvement by substituting Warhurst's relation.
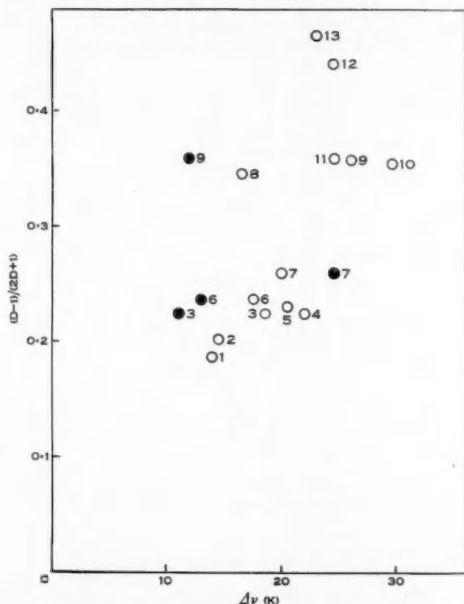

Fig. 2.—Frequency displacements in relation to D function. ○ Acetone C=O fundamental. ● Chloroform C—H fundamental.

Further consideration of the results requires an analysis of what is a complex theoretical situation. Equation (1) is an expression of the relation of $\Delta\nu$ to the electrostatic polarization of the solvent by the solute dipole. This electrostatic interaction is certainly the most important of the physical forces between solute and solvent, and as mentioned in the Introduction we believe that chemical or quasi-chemical solute-solvent interactions are unlikely to be significant in the cases under discussion. The effect on the solute dipole of solvent polarization can be expressed by the Onsager (1936) reaction field, which has two components,

one due to electron polarization and one to solvent dipole orientation. (We assume that atom polarization can be neglected.) As pointed out by Bauer and Magat (1938), the use of the static value of D in (1) is justified only if both polarization components follow at every instant the changes in the solute dipole resulting from its thermal libration, vibration, and vibrational transitions. (The last named changes, though small, are probably not negligible (Gordy, Smith, and Trambarulo 1953).) While this condition is met by the electronic component, it is not by the orientation component since dipole orientation relaxation times in the liquid state are of the order of 10^{-11} sec (Whiffen 1950),

TABLE 5

C=O FIRST OVERTONE

State	Acetone		Diisopropyl Ketone		Acetaldehyde	
	ν (K)	$\Delta\nu$ (K)	ν (K)	$\Delta\nu$ (K)	ν (K)	$\Delta\nu$ (K)
Vapour	3456	—	3443	—	3472	—
Solvents						
1. n-Hexane	3430	26	3420	23	3451	21
2. cycloHexane	3423	33	3414	29	3449	23
3. Carbon tetrachloride	3420	36	3409	34	3442	30
4. Dioxan	3415	41	3408	35	3433	39
5. Benzene	3415	41	3406	37	3436	36
6. Tetrachloroethylene	3421	35	3411	32	3444	28
7. Carbon disulphide	3417	39	3407	36	3438	34
8. Diethyl ether	3423	33	3416	27	3442	30
9. Chloroform	3404	52	3394	49	3430	42
10. Bromoform	3399	57	3388	55	—	—
11. Ethylene dibromide	3410	46	3400	43	3430	42
12. Pyridine	3409	47	3398	45	3427	45
Pure liquid	3414	42	3407	36	—	—

which is some thousand times greater than molecular vibration periods. For this reason, Bauer and Magat (1938) stated that a suitable high frequency value of D should be used in (1). At this point it should be noted that the successful correlations between $\Delta\nu$ and the D function by Jones and Badger (1951) for O−H and by West and Edwards (1937) for HCl were obtained in solvents that either were non-polar or else had small dipole moments, where there is little difference between D and n^2 (see next paragraph).

There is an advantage in considering the electronic and orientation components as exerting separate and superimposed effects. In non-polar solvents, we are concerned only with the electron polarization,* whose effect can be

* This statement needs qualification, since the zero dipole moment of a non-polar solvent may be the resultant of symmetrically directed strong local dipoles (e.g. CCl_4). Such a molecule may well behave as polar towards a solute molecule in its immediate neighbourhood in the liquid state, although it is effectively non-polar towards more distant molecules.

TABLE 6

C—H FUNDAMENTAL—CHLOROFORM

State	ν (K)	$\Delta\nu$ (K)	$\varepsilon_{max.}$	$\Delta\nu_{\frac{1}{2}}$	Intensity
Vapour	3033	—	—	—	—
Solvents					
3. Carbon tetrachloride ..	3022·0	11	7·6	15	174
6. Tetrachloroethylene ..	3020·0	13	8·0	15	184
7. Carbon disulphide	3008·5	24·5	9·7	12	203
9. Chloroform (liquid)	3021	12	—	—	—

described by replacing D in equation (1) by n^2, where n is the solvent refractive index at the appropriate frequency, as in the equation proposed by one of us for electronic spectra (Bayliss 1950).

$$\Delta\nu = \frac{C'(n^2-1)}{2n^2+1}. \quad \dots\dots\dots\dots\dots\dots \quad (2)$$

The factor C' depends on the model; for a point dipole in a spherical cavity of radius a, and for a transition of oscillator strength f, it is given by
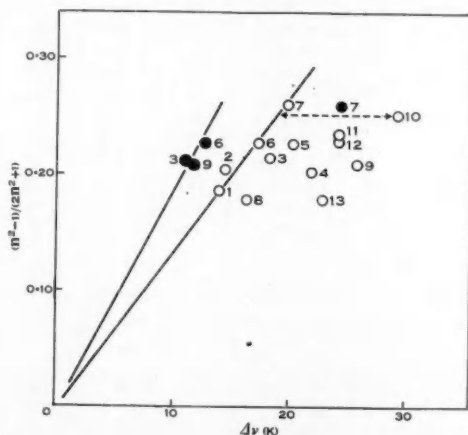
$$C' = \frac{f}{\nu a^3} \times 10^{10}. \quad \dots\dots\dots\dots\dots\dots \quad (3)$$

Fig. 3.—Frequency displacements plotted against n function. ○ Acetone C=O fundamental. ● Chloroform C—H fundamental. For C=O in bromoform (10) we have indicated the " deviation " (see text).

In polar solvents, we expect an electronic component of $\Delta\nu$ as given by (2), and a superimposed orientation component for which no simple theory exists.

In Figure 3 we have plotted $\Delta\nu$ against the n function of equation (2) for the C=O and C—H fundamentals in acetone and chloroform respectively.

Strictly speaking we should use infra-red refractive indices ; but since we could locate values of these for only four solvents (see Table 8) we have for uniformity used values of n at the line Hα.   It is seen from Table 8 that the diagram would be changed very little if infra-red n values were used for the four solvents concerned.   Now there are certain features of Figure 3 that acquire additional significance when they are considered in conjunction with the intensities (see Section III (c)).   For the C=O vibration the points in the non-polar solvents n-hexane (1), *cyclo*hexane (2), tetrachloroethylene (6), and carbon disulphide (7) lie on a straight line through the origin as required by equation (2).   It seems significant that all the other C=O points lie to the right of this line, that is, to greater $\Delta\nu$, suggesting that the line measures the electronic polarization component of $\Delta\nu$, and that the horizontal displacements from this line (which we

TABLE 7
C—C FUNDAMENTAL—ACETONITRILE

State	ν (K)	$\Delta\nu$ (K)	ε_{max}.	$\Delta\nu_{\frac{1}{2}}$	Intensity
Vapour	919	—	—	—	—
Solvents					
2. *Cyclo*hexane	918*	1	—	—	—
3. Carbon tetrachloride ..	918·5	0·5	6·6	7	79
5. Benzene	917	2	5·2	7·5	69
7. Carbon disulphide	918	1	5·2	7·5	67
9. Chloroform	918·5	0·5	9·0	6	93
10. Bromoform	919	0	9·1	7·5	111
11. Pyridine	917	2	6·3	7	82
13. Acetone	917	2	—	—	—
Acetonitrile (liquid)	918	1	—	—	—

* This measurement is only approximate because of high solvent absorption.

call " deviations ", see Fig. 3) are a measure of the additional superimposed components of $\Delta\nu$.   The greatest deviations are in solvents of relatively high dipole moment where the orientation component should be greatest, namely, bromoform (10), chloroform (9), and acetone (13).   The non-polar solvent carbon tetrachloride (3) shows a small deviation which could arise from its local bond moments.   Non-polar benzene (5) also gives a small deviation which is more difficult to explain since the individual C—H bond moments are probably small.   However, a detailed theory would have to consider the electronic polarization anisotropy of benzene, which could introduce what is effectively an orientation component.

The other C=O frequencies, not shown in Figure 3, conform to the discussion of the preceding paragraph.   The chloroform C—H fundamental, on the other hand, still behaves rather inexplicably.   The application of equation (2) in Figure 3 shows a considerable improvement over that of equation (1) in Figure 2 ; but the results are still not linear through the origin, and non-polar carbon disulphide (7) appears to show a deviation while polar chloroform (9) does not.

However, it is considered that these discrepancies, in a subject which has many theoretical difficulties, do not invalidate the attempt to consider frequency shifts as the sum of separate components.

The completely quantitative application of equation (2) including the value of C' as given by (3), requires that the cavity radius a should have a value of $1 \cdot 2$ Å for acetone, $1 \cdot 3$ Å for diisopropyl ketone, and $0 \cdot 7$ Å for chloroform. These are similar to the a values that have been found in the application of (2) to electronic spectra (Bayliss 1950 ; Bayliss and Hulme 1953) and are reasonable if the cavity relates to the absorbing group.

TABLE 8

DIELECTRIC CONSTANTS, REFRACTIVE INDICES, AND DIPOLE MOMENTS

Solvents	D^*	$n(\mathrm{H}\alpha)\dagger$	$\dfrac{D-1}{2D+1}$	$\dfrac{n^2-1}{2n^2+1}$	$\mu\ddagger$ (D)
1. n-Hexane	$1 \cdot 904$	$1 \cdot 373$	$0 \cdot 188$	$0 \cdot 186$	0
2. cycloHexane	$2 \cdot 025$	$1 \cdot 424$	$0 \cdot 203$	$0 \cdot 204$	0
3. Carbon tetrachloride	$2 \cdot 234$	$1 \cdot 457$	$0 \cdot 226$	$0 \cdot 214$	0
,, ,, ...		$1 \cdot 436\S$		$0 \cdot 207\S$	
4. Dioxan	$2 \cdot 235$	$1 \cdot 420$	$0 \cdot 226$	$0 \cdot 202$	$0\text{--}0 \cdot 4$
5. Benzene	$2 \cdot 283$	$1 \cdot 496$	$0 \cdot 231$	$0 \cdot 226$	0
6. Tetrachloroethylene	$2 \cdot 365$	$1 \cdot 501$	$0 \cdot 238$	$0 \cdot 227$	0
7. Carbon disulphide	$2 \cdot 633$	$1 \cdot 618$	$0 \cdot 261$	$0 \cdot 260$	0
,, ,, ...		$1 \cdot 61\S$		$0 \cdot 257\S$	
8. Diethyl ether	$4 \cdot 376$	$1 \cdot 351$	$0 \cdot 346$	$0 \cdot 178$	$1 \cdot 1$
9. Chloroform	$4 \cdot 813$	$1 \cdot 443$	$0 \cdot 359$	$0 \cdot 209$	$1 \cdot 1$
,, ...		$1 \cdot 422\|$		$0 \cdot 203\|$	
10. Bromoform	$4 \cdot 73$	$1 \cdot 592$	$0 \cdot 357$	$0 \cdot 252$	$1 \cdot 3$
,, ...		$1 \cdot 558\|$		$0 \cdot 244\|$	
11. Ethylene dibromide ..	$4 \cdot 865$	$1 \cdot 534$	$0 \cdot 360$	$0 \cdot 237$	$1 \cdot 0$
12. Pyridine	$12 \cdot 4$	$1 \cdot 505$	$0 \cdot 442$	$0 \cdot 229$	$2 \cdot 2$
13. Acetone	$21 \cdot 40$	$1 \cdot 357$	$0 \cdot 466$	$0 \cdot 179$	$2 \cdot 7$

* Timmermans (1950) ; Landolt-Börnstein (1936) ; Weissberger and Proskauer (1935).

† Timmermans (1950).

‡ Landolt-Börnstein (1951).

§ Infra-red value (Pfund 1935). The CS_2 value is an average in the relevant infra-red region ; the actual n for CS_2 at 1800 K is only $1 \cdot 51$, but this point is in the lower limb of a region of marked anomalous dispersion.

‖ Infra-red value (Pittman 1939).

(c) Intensities

There have been relatively few experimental studies of solvent effects on infra-red intensities, and there is no adequate theory. We have therefore used our results to search for some correlation between intensity and some solvent property. If the classical theory of Chako (1934) were applicable, the intensity would be related to solvent refractive index n. These quantities are plotted in Figure 4, where there is a linear relation for chloroform $C-H$ in the few solvents measured ; but on the other hand there is no simple relation between intensity and n for the acetone $C=O$. The existence of a simple relation might have been

deduced had the measurements not included carbon disulphide (7) and chloroform (9) as solvents, emphasizing the need to use as many different solvents as possible. We could likewise find no simple correlation between intensity and solvent D. If in terms of Section III (b) it is legitimate to regard the solvent
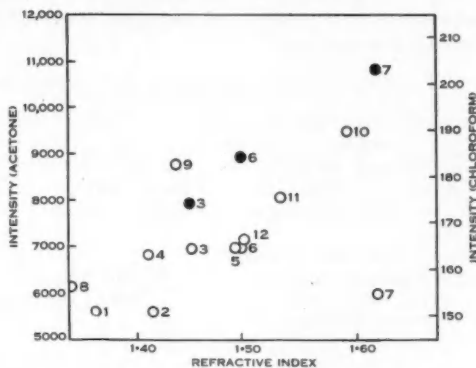

Fig. 4.—Intensities (for units see text) in relation to solvent refractive index. ○ Acetone C=O fundamental. ● Chloroform C—H fundamental.

effect as the sum of electronic and orientation contributions, then it would be expected that these might separately affect the intensities. Furthermore there is only a small spread in the intensities amongst the normal non-polar solvents
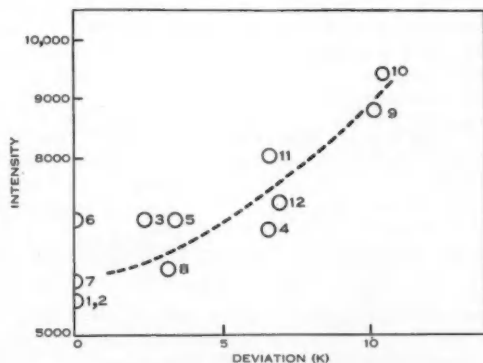
Fig. 5.—Intensity of acetone C=O fundamental in relation to " deviation " (see text and Fig. 3).

of Figure 3, suggesting that the greatly increased intensity in some dipolar solvents is the result of the orientation contribution to the reaction field. In Figure 5 we have plotted, for the acetone C=O fundamental, the intensity

c

against the " deviation " measured from Figure 3.   It is seen that there is a definite, although imperfect, correlation for which we offer at present no theoretical reason.   Further work on this subject is in progress.

IV. ACKNOWLEDGMENT

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THE CALCULATION OF ATOMIC POLARIZATIONS FOR BENZENE AND CERTAIN OTHER POLYATOMIC MOLECULES

By R. J. W. Le Fèvre* and D. A. A. S. Narayana Rao*

Summary

Formulae are presented for the *a priori* computation of the atomic polarizations of the following molecular types: X_2YZ (linear), XY_2Z_2 (tetrahedral), XZY_3 (tetrahedral), X_2Y_6, and X_6Y_6 (plane hexagonal). Comparison is made between calculation and experiment for 21 compounds. Bond moments are calculated for four compounds from $_AP$ expt.

New determinations of total polarization as vapours are recorded for benzene, *p*-xylene, mesitylene, *p*-dichlorobenzene, *p*-dibromobenzene, diphenyl, *cyclo*hexane, 1,4-dioxane, tetrachloroethylene, naphthalene, and hexachlorobenzene.

A rough additivity is shown to exist among the values of $(_EP + _AP)$ for 26 benzenoid molecules containing —Cl, —Br, =O, —NO₂, —CN, and —CH₃ as substituents.

I. Introduction

Le Fèvre and Rao (1954) showed that a general method of computing atomic polarizations consists in forming an equation for the potential energy of a molecule and applying the condition that this is a minimum at equilibrium. Equations, in terms of bond lengths, intervalency angles, link moments, and force constants, were given for 10 types of polyatomic structures. The $_AP$'s predicted compared reasonably well with those from experiment. The present paper extends the study to five further general structures. Appropriate formulae, developed by arguments following those detailed previously, are set out *seriatim* in Section II.

II. New Formulae for Atomic Polarizations of Specified Structures

(a) X_6Y_6 (Plane Hexagonal)

$$_AP = \frac{24\pi Ne^2}{9q} + \frac{24\pi N\mu^2}{9Hl^2} + \frac{18\pi N\mu^2}{9(K+k)a^2} + \frac{24\pi N\mu^2}{9hl^2},$$

where q, H, K, k, h are the force constants in the potential energy term assumed by Wilson (1934), and a and l are the bond lengths XX and XY respectively.
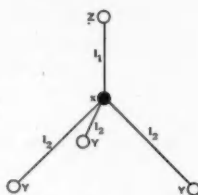
* School of Chemistry, University of Sydney.

(b) XZY_3 (assuming All Angles to be Tetrahedral)

$$_AP = \frac{4\pi N e_1^2}{9k_1} + \frac{4\pi N e_2^2}{27k_2} + \frac{32\pi N}{27k_2}\left[\frac{3e_2 b + e_1(l_1/l_2)a}{3b+a}\right]^2 + \frac{32\pi N \mu_2^2}{27(k_\delta + k_{\delta'})}$$

$$+ \frac{16\pi N}{27}\left(\frac{1}{k_\delta} + \frac{1}{k_{\delta'}}\right)\left(\frac{3\mu_2 b + \mu_1 a}{3b+a}\right)^2,$$

where

$$a = \frac{1}{l_1}\left[\frac{m_y}{m_z}\frac{l_2}{l_1} + \frac{m_y}{m_x}\left(\frac{3l_1+l_2}{l_1}\right)\right],$$

$$b = \frac{1}{l_2}\left[1 + \frac{m_y}{m_x}\left(\frac{3l_1+l_2}{l_1}\right)\right],$$

and k_δ and $k_{\delta'}$ are respectively the angular force constants of angles YXY and YXZ.
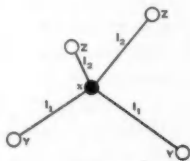
(c) XY_2Z_2 (with Tetrahedral Angles)

$$_AP = \frac{8\pi N e_1^2}{27k_1} + \frac{8\pi N e_2^2}{27k_2} + \frac{16\pi N}{27}\left(\frac{e_1 A^1 + e_2 B^1}{l_2 A^1 + l_1 B^1}\right)^2 \frac{l_2^2}{k_1}$$

$$+ \frac{16\pi N}{27}\left(\frac{e_2 A^{11} + e_1 B^{11}}{l_1 A^{11} + l_2 B^{11}}\right)^2 \frac{l_1^2}{k_2}$$

$$+ \frac{16\pi N}{27 k_{\delta'}}\left\{\left(\frac{l_2\mu_1 A^1 + l_1\mu_2 B^1}{l_2 A^1 + l_1 B^1}\right)^2 + \left(\frac{l_1\mu_2 A^{11} + l_2\mu_1 B^{11}}{l_1 A^{11} + l_2 B^{11}}\right)^2\right\}$$

$$+ \frac{8\pi N}{27}\left[\frac{4k_{\delta_1}\mu_1^2 + 4k_{\delta_2}\mu_2^2 + k_{\delta'}(\mu_1+\mu_2)^2}{4k_{\delta_1}k_{\delta_2} + k_{\delta'}(k_{\delta_1}+k_{\delta_2})}\right],$$

where

$$A^1 = 1 + \frac{2m_y}{m_x}\left(\frac{l_1+l_2}{l_2}\right), \qquad B^1 = \frac{m_y}{m_z}\frac{l_1}{l_2} + \frac{2m_y}{m_x}\left(\frac{l_1+l_2}{l_2}\right);$$

$$A^{11} = 1 + \frac{2m_z}{m_x}\left(\frac{l_1+l_2}{l_1}\right), \qquad B^{11} = \frac{m_z}{m_y}\frac{l_2}{l_1} + \frac{2m_z}{m_x}\left(\frac{l_1+l_2}{l_1}\right);$$

and k_{δ_1}, k_{δ_2}, and $k_{\delta'}$ are respectively the angular force constants associated with the angles YXY, ZXZ, and YXZ.
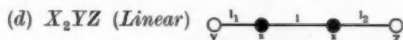
(d) X_2YZ (Linear)

Fig. 3

$$P = \frac{4\pi N}{9}\left\{ \frac{2}{k_{\delta_1}}\left[\frac{(2B/l)\mu_2 + \mu_1(AB^1 + BA^1 + 2A/l)}{AB^1 + BA^1 + 2A/l + 2B/l} \right]^2 + \frac{2}{k_{\delta_2}}\left[\frac{(2A/l)\mu_1 + \mu_2(AB^1 + BA^1 + 2B/l)}{AB^1 + BA^1 + 2A/l + 2B/l} \right]^2 \right\}$$

$$+ \frac{4\pi Ne_1^2}{9k_1} + \frac{4\pi Ne_2^2}{9k_2},$$

where

$$A^1 = \left(1 + \frac{m_x}{m_y}\frac{l}{L}\right)\frac{1}{l_1}, \qquad A = 1 + \frac{m_x}{m_y}\left(\frac{2l_2+l_1}{L}\right)\frac{1}{l_1} \qquad L = l_1 + l_2 + l;$$

$$B^1 = \left(1 + \frac{m_x}{m_z}\frac{l}{L}\right)\frac{1}{l_2}, \qquad B = 1 + \frac{m_x}{m_z}\left(\frac{2l_1+l_2}{L}\right)\frac{1}{l_2}.$$

The contribution to $_AP$ from the stretching of the bonds is taken as an approximation to be

$$\frac{4\pi Ne_1^2}{9k_1} + \frac{4\pi Ne_2^2}{9k_2}.$$

(e) X_2Y_6

$$_AP = \frac{64\pi N\mu^2}{27(k_{\delta} + k_{\delta'})} + \frac{32\pi N\mu^2}{27}\left(\frac{1}{k_{\delta}} + \frac{1}{k_{\delta'}}\right) + \frac{24\pi Ne^2}{9k_1}.$$

This formula is suggested by analogies.

III. Numerical Applications

The halogenated methanes are considered in Table 1. The force constants are taken from Herzberg (1945). The angular force constants between similar bonds are assumed to be the same as those in the corresponding tetrahedral molecules. The atomic polarizations from infra-red absorptions are calculated from the relation

$$_AP = \sum_i \frac{V_0 A_{\nu_i}}{3\pi^2 c \nu_i^2},$$

where V_0 is the molar volume at N.T.P., A_{ν_i} is the intensity of the infra-red absorption band, of frequency ν_i (in wave numbers), in c/s cm at N.T.P. Data

TABLE 1

CALCULATION OF AP FOR HALOGENATED METHANES

Molecule	$l_1 \times 10^8$	$l_2 \times 10^8$	$\mu_1 \times 10^{18}$	$\mu_2 \times 10^{18}$	$k_1 \times 10^{-5}$	$k_2 \times 10^{-5}$	$k\delta \times 10^{12}$	$k\delta' \times 10^{12}$	AP Calc.	AP From Infra-red Studies	AP Expt.	EP
CH_3F	1·36	1·08	2·25	0·4	9·14	5·04	5·37	8·86	0·16	0·39	2·9±0·6,[6] 0·5[2]	6·7Σ D
CH_3Cl	1·76	,,	2·26	,,	4·38	,,	,,	6·76	,,	0·19	2·3±0·5,[4] 2·9±0·5[5]	11·21 Vap.
CH_3Br	1·93	,,	2·2	,,	3·36	,,	,,	6·06	,,	0·18	0·6±1·1,[6] 3·2±1·3[7] 0·1±0·4[1]	14·6Σ D
CH_3I	2·12	,,	2·03	,,	2·5	,,	,,	5·25	0·16	0·13	1·6±0·5,[6] 0·15±1·1[8]	18·45 Liq.
CH_2F_2	1·08	1·36	0·4	2·07	5·04	9·14	5·37 / 13·2	8·86	0·50			
CH_2Cl_2	,,	1·76	,,	1·76	,,	4·38	5·37 / 10·25	6·76	0·41		2·7,[2] 4·0±0·7[3]	16·04 Vap.
CH_2Br_2	,,	1·93	,,	1·64	,,	3·36	5·37 / 8·83	6·06	0·38		0·7±0·8,[11] 1·3±1·3[3]	22·21 Vap.
CHF_3	,,	1·36	,,	2·0	,,	9·14	13·2	8·86	0·64		1·8[9]	7·0 Vap.
$CHCl_3$	,,	1·76	,,	1·42	,,	4·38	10·25	6·76	0·41		3·8, 4·3[3]	21·05 Vap.
$CHBr_3$	,,	1·93	,,	1·4	,,	3·36	8·83	6·06	0·45		0·45±2·0[11]	29·15 Liq.

[1] Buckingham and Le Fèvre (1953). [2] Ramaswamy (1936). [3] Maryott, Hobbs, and Gross (1941). [4] Fuchs (1930). [5] Sanger, Steiger, and Gächter (1932). [6] Smyth and McAlpine (1934a). [7] Groves and Sugden (1937a). [8] Le Fèvre and Rao (1955). [9] Ramaswamy (1935a, 1935b).

for infra-red intensities are from Barrow and McKean (1952). The bond moments are chosen arbitrarily to correspond to the moment of the molecule.

The atomic polarizations computed by our new equations (column headed : $_AP$ calc.) and those from infra-red intensities (column headed : $_AP$ from infra-red) are in good agreement for the four methyl halides. With the remaining instances comparison must be made between the $_AP$ calc. and the figure given under the

TABLE 2

CALCULATIONS OF $_AP$ FOR VARIOUS MOLECULES

Molecule	$l \times 10^8$	α	$\mu \times 10^{18}$	$k \times 10^{-5}$	$k_d \times 10^{12}$	$_AP$ Calc.	$_AP$ Expt.
HCN	$l_1=1·06$ $l_2=1·15$		$\mu_1=0·4$ $\mu_2=3·3$	$k_1=5·8$ $k_2=17·9$	$2·5$	$0·52$	$0\pm1·2$ [1]
D₂O	$0·96$	$52°\,30'$	$1·53$	$7·94$	$6·5$	$0·25$	$0\pm1·2$ [6]
CH₃CN	$l_1=1·5$ $l_2=1·16$		$\mu_1=1$ $\mu_2=3$	$k_1=5·2$ $k_2=17·9$	$3·0$	$1·2$	$0\pm3·1$ [7]
C₂Cl₄	$1·72$	$57°$	$1·9$	$3·21$	$k\delta=18·6$ $k\delta'=14·8$ $k\beta=5·9$	$1·75$	$2·2$ [2]
COCl₂	$l_1=1·28$ $l_2=1·68$	$58°\,30'$	$\mu_1=2·85$ $\mu_2=1·6$	$k_1=12·3$ $k_2=2·43$	$k\delta=21·3$ $k\delta'=3·68$ $k\Delta=3·14$	$2·0$	$1·8\pm0·4$ [1]
COS	$l_1=1·56$ $l_2=1·16$		$\mu_1=2·7$ $\mu_2=2·0$	$k_1=8·0$ $k_2=14·2$	$6·6$	$1·35$	$1·6\pm0·2$ [3]
C₂F₆	$1·36$		$2·0$	$9·14$	$k\delta=k\delta'=13·2$	$2·2$	6 [4]
PCl₃	$2·0$	$\alpha=50°\,30'$ $\beta=63°$	$0·57$	$2·25$	$13·8$	$0·1$	6 [8]
PH₃	$1·42$	$\alpha=46°\,30'$ $\beta=57°$	$0·34$	$3·09$	$6·66$	$0·03$	$1·4$ [9]
AsCl₃	$2·16$	$\alpha=50°\,30'$ $\beta=63°$	$1·17$	$2·1$	$10·7$	$0·34$	9 [5]
C₂HCl	$l_1=1·68$ $l=1·21$ $l_2=1·06$		$\mu_1=1·5$ $\mu_2=1·05$	$k_1=5·2$ $k_2=5·9$	$k\delta_1=5$ $k\delta_2=3·3$	$1·1$	$1·0$ [10]
C₂HBr	$l_1=1·80$ $l=1·21$ $l_2=1·06$		$\mu_1=\mu_2$ $=1·05$	$k_1=4·2$ $k_2=5·9$	$k\delta_1=5$ $k\delta_2=3·3$	$0·97$	$1·4$ [10]

[1] Smyth and McAlpine (1934b). [2] Present work. [3] Zahn and Miles (1928). [4] Fuoss (1938). [5] Grassi and Puccianti (1937). [6] Groves and Sugden (1935). [7] Groves and Sugden (1937a). [8] Grassi (1933). [9] Watson (1927). [10] Brockway and Coop (1938).

heading $_AP$ expt., derived by subtracting the $_EP$ reported in the last column of Table 1 from the appropriate distortion polarization, $_DP$, shown by dielectric constant measurements ; $_EP$ is the molecular refraction extrapolated for infinite wavelength in the vapour or liquid phase, as indicated, except for CH₃F and CH₃Br for which the $_EP$'s quoted are the summed atomic refractions for the sodium D line (from Landolt-Börnstein 1936).

For a given substance $_AP$ expt. is seen to vary widely with different observers. Except for CH_2Br_2 and $CHBr_3$, where the congruence between $_AP$ calc. and $_AP$ expt. is satisfactory, $_AP$ expt. usually considerably exceeds $_AP$ calc. Now, while from infra-red studies (Schatz and Hornig 1953) it is known that the effective charge during the stretching vibration of the $C-F$ bond is much higher than μ/l, and that therefore the atomic polarizations of fluorinated methanes could be about twice those calculated above, the corresponding indications are that with the other compounds true atomic polarizations should not differ by more than 20 to 30 per cent. from the calculated values. We suspect that most $_AP$ expt. data are erroneously high.

The cases of 12 other compounds are given in Table 2. The force constants for HCN, D_2O, COS, PCl_3, PH_3, and $AsCl_3$ are from Herzberg (1945), and for CH_3CN, C_2Cl_4, $COCl_2$, they are calculated from the vibrational frequencies

TABLE 3

CALCULATION OF BOND MOMENTS FROM $_AP$

Molecule	$_AP$	$l \times 10^8$	$k \times 10^{-5}$	$k_\delta \times 10^{12}$	μbond $\times 10^{18}$ Calc.	μbond From Infra-red Studies
SO_2	$1 \cdot 65^{(5)}$	$1 \cdot 43$	$10 \cdot 8$	$k_\delta = 9 \cdot 4$ $k_\Delta = 32 \cdot 7$	$3 \cdot 05$	
C_2H_6	$0 \cdot 09^{(1)}$	$1 \cdot 08$	$5 \cdot 0$	$k_\delta = 5 \cdot 4$ $k_{\delta'} = 6 \cdot 4$	$0 \cdot 27$	$0 \cdot 1, 0 \cdot 34, 0 \cdot 28^{(3)}$
Si_2H_6	$4 \cdot 38^{(1)}$	$1 \cdot 46$	$2 \cdot 84$	$k_\delta = k_{\delta'} = 4 \cdot 03$	$1 \cdot 54$	
C_6H_6	$0 \cdot 8^{(2)}$	$l = 1 \cdot 08$ $a = 1 \cdot 39$	$K = 7 \cdot 61$ $q = 5 \cdot 06$	$hl^2 = 2 \cdot 62$ $ka^2 = 13 \cdot 7$ $Hl^2 = 8 \cdot 0$	$0 \cdot 55$	$0 \cdot 57^{(4)}$

[1] Watson and Ramaswamy (1936). [2] Present paper. [3] Thorndike (1947). [4] Cole and Thompson (1950). [5] Smits, Moerman, and Pathius (1937).

(CH_3 is considered a point in the case of CH_3CN). In C_2F_6, k_δ and $k_{\delta'}$ are taken to be the same as for the angle FCF in CF_4. In C_2HCl and C_2HBr the angular force constant HCC is taken to be the same as in C_2H_2 and that for $Cl-C-C$ or $Br-C-C$ is taken to be of the order 5×10^{-12}, from analogies. The agreement between the calculated and experimental values of $_AP$ is quite satisfactory except in the cases of C_2F_6 and the pyramidal molecules PCl_3, PH_3, and $AsCl_3$. With C_2F_6 the calculated value could be too low for the reason previously mentioned for the $C-F$ bond, but in each of the other three cases, even were the inadequacy in the computation of that part of the atomic polarization due to stretching vibrations to require for its correction a doubling of the $_AP$ calc., the result would still be far from the—therefore questionable—experimental value.

Finally, Table 3 deals with the reversed application of our formulae to four molecules in which component bond moments are calculated from the experimental values of $_AP$. For C_2H_6 the force constants are taken from Herzberg

TABLE 4
MEASUREMENTS

Vapour	Temp. (°C)	x/x'	DP (o.c.)	p (Range cm Hg)	No. of Observations	DP Av.	EP	AP	DP Other Observers
Benzene	24	3·698	27·15	5–8	10				
	66	3·642	26·74	10–11	12	27·0	26·2 Vap.	0·8	26·9[1] 26·2,[2] 27·1,[3] 27·1[4]
	127	3·659	26·86	12–23	12				
	139	3·666	26·91	11–14	10				
	227	3·710	27·26	16–30	16				
p-Xylene	135	5·094	37·4	10–22	9				
	155	5·054	37·1	11–22	9	37·1	34·6 Liq.	2·5	37·7[4]
	166	5·081	37·3	10–21	12				
	206	5·025	36·9	13–30	12				
Mesitylene	147	5·857	43·0	6–11	11				
	180	5·857	43·0	7–20	8	42·6	39·2 Liq.	3·4	—
	194	5·761	42·3	7–20	13				
	192	5·735	42·1	8–15	11				
	206	5·814	42·7	8–15	9				
p-C6H4Cl2	194	5·244	38·5	9–20	16				
	195	5·189	38·1	9–16	12	38·1	34·8 Liq.	3·3	38·1[5]
	200	5·135	37·7	6–14	11				
	230	5·189	38·1	9–16	12				

TABLE 4 (*Continued*)

Vapour	Temp. (°C)	x/x'	D^P (c.c.)	p (Range cm Hg)	No. of Observations	D^P Av.	E^P	A^P	D^P Other Observers
p-$C_6H_4Br_2$	198	6·061	44·5	8–10	10	44·3	40·1	4·2	—
	195	5·980	43·9	8–11	11				
	198	6·047	44·4	6–11	11				
	228	5·939	43·6	7–13	9				
	214	6·115	44·9	8–13	9				
Diphenyl	212	7·464	54·8	6–13	9	54·3	49·5 Liq.	4·8	—
	214	7·302	53·6	3–6	20				
	232	7·382	54·2	6–12	14				
	225	7·355	54·0	7–9	10				
cycloHexane	92	3·740	27·45	10–26	11	27·5	27·1 Liq.	0·4	—
	115	3·750	27·53	11–33	12				
	195	3·748	27·52	15–29	12				
1,4-Dioxane	95	3·366	24·71	11–14	13	24·65	21·13 Liq.	3·5	24·5,[6] 26·0[7]
	123	3·357	24·65	12–22	12				
	183·5	3·341	24·53	14–33	13				
C_2Cl_4	134	4·304	31·6	10–30	12	31·6	29·3 Liq.	2·3	—
	148	4·304	31·6	10–30	11				
	165	4·290	31·5	12–20	12				
	180	4·304	31·6	10–20	11				

TABLE 4 (*Continued*)

Vapour	Temp. (°C)	x/x'	DP (c.c.)	p (Range cm Hg)	No. of Observations	DP Av.	EP	AP	DP Other Observers
Naphthalene ..	208	6·170	45·3	7–10	8				
	218	6·156	45·2	8–11	11	45·4	41·8 Liq.	3·6	—
	218	6·238	45·8	8–10	11				
C_6Cl_6* ..	304	2·233	60·3	6–11	13				
	271	2·245	60·6	7–11	6	60·6	53·4	7·2	—
	281	2·241	60·5	5–14	12				
	288	2·262	61·1	9–13	8				

* The polarization of C_6Cl_6 is measured with reference to benzene for which the value is taken as 27·0.

[1] McAlpine and Smyth (1933).   [2] Groves and Sugden (1934).   [3] Ramaswamy (1936).   [4] Hurdis and Smyth (1942a, 1942b).   [5] Groves and Sugden (1937b).   [6] Schwingel and Greene (1934).   [7] Kubo (1936).

TABLE 5

ADDITIVITY OF DISTORTION POLARIZATION

Compound	$_DP$ Of Group X Replacing Hydrogen	Calc.	Obs.	State	Reference
C_6H_6			27·0	Vapour	Present paper
s-$C_6H_3(CH_3)_3$ ..	5·2		42·6	,,	,, ,,
C_6Cl_6	5·6		60·6	,,	,, ,,
p-$C_6H_4Br_2$ ..	8·65		44·3	,,	,, ,,
p-$C_6H_4O_2$	9·8		36·6	,,	Coop and Sutton (1938) .
p-$C_6H_4(NO_2)_2$ ..	9·75		46·5	,,	,, ,, ,,
p-$C_6H_4(CN)_2$ ..	10·7		48·4	,,	,, ,, ,,
$C_6H_5(CH_3)$ ..		32·2	32·2±0·4	,,	McAlpine and Smyth (1933)
p-$C_6H_4(CH_3)_2$ ..		37·4	37·1	,,	Present paper
C_6H_5Cl		32·6	31·5±0·7	,,	McAlpine and Smyth (1935)
p-$C_6H_4Cl_2$		38·2	38·1	,,	Present paper
C_6H_5Br		35·65	34·8±1·5	,,	Le Fèvre and Rao (1955)
$C_6H_5NO_2$		36·75	37·2±5·4	,,	McAlpine and Smyth (1935)
p-$C_6H_4(NO_2)(CN)$		47·5	47·5	,,	Coop and Sutton (1938)
$C_6H_2O_2(CH_3)_2$* ..		47·0	47·4	,,	,, ,, ,,
$C_6H_2O_2Cl_2$* ..		47·8	46·3	,,	,, ,, ,,
$C_6(CH_3)_6$ ..		58·2	55·8	Solution	Tiganik (1931)
s-$C_6H_3Cl_3$ ..		43·8	43·0	,,	,, ,,
s-$C_6H_3Br_3$ ..		52·95	52·0	,,	,, ,,
s-$C_6H_3(NO_2)_3$ ..		56·25	55·0	,,	Le Fèvre and Le Fèvre (1935)
$C_6H_2O_2Br_2$ ..		53·9	54·0	,,	Hammick, Hampson, and Jenkins (1938)
Trichloromesitylene		59·4	58·9	,,	Tiganik (1931)
Tribromomesitylene		68·55	66·3	,,	,, ,,
Trinitromesitylene		71·85	70·5	,,	Le Fèvre and Le Fèvre (1935)
			72·2	,,	Jenkins (1936)
s-$C_6Cl_3(NO_2)_3$ ..		73·05	68·5	,,	Tiganik (1931)
s-$C_6Br_3(NO_2)_3$ ..		82·2	77·6	,,	,, ,,
			91±2	,,	Lütgert (1931)

* Derivatives of 1,4-benzoquinone.

(1945), and in the case of Si_2H_6, the angular constants $H-Si-H$ and $H-Si-Si$ are assumed to be the same and equal to that for $H-Si-H$ in SiH_4. The force constants for benzene are from Garforth, Ingold, and Poole (1948). The The μ_{bond} values in the case of C_2H_6 and C_6H_6 are of the same order as obtained

from infra-red intensity studies and the Si—H bond moment in Si_2H_6 is nearly the same as the Si—H bond moment in SiH_4 calculated by Le Fèvre and Rao (1954).

IV. Measurements

The polarizations of 11 substances at various temperatures, and determined in all cases but one relatively to carbon dioxide, are given in Table 4. The apparatus employed, method and symbols used, are as described by Le Fèvre (1953, Ch. 2).

V. Discussion

The atomic polarization of *cyclo*hexane seems to be of the order of half that of benzene, although the number of dipoles is double ; this contrast may be due to a tighter coupling of the bonds, and/or a smaller magnitude of the C—H bond moment in the former molecule ; whatever the cause it is a warning against the general belief that $_AP$ inevitably increases with the number of bonds.

With *cyclo*hexane, dioxane, and tetrachloroethylene the distortion polarizations in the liquid and vapour states are practically the same, and so the $_AP$ obtained by subtracting $_EP$ in the liquid state, should be correct. For benzene, $_EP$ in the vapour state is available. In the other cases absence of data for vapours has compelled us to take molar refractions, R, in the liquid state as an approximation to $_EP$. Since usually $R_{vap.}$ slightly exceeds $R_{liq.}$, the $_AP$'s in Table 4 quoted with the annotation " liq." under $_EP$ may be taken as maximum estimates.

The distortion polarizations of 26 substances are assembled in Table 5. The first seven compounds are utilized to provide by subtraction the apparent change in $_DP$ caused by the replacement of hydrogen in benzene by various atoms or groups. These differences, in conjunction with $_DP_{C_6H_6}=27\cdot0$ c.c., lead to the figures under $_DP$ calc. Thus calculated and observed distortion polarizations are compared for nine compounds studied in the vapour phase, and 10 compounds in solution (benzene).

Agreement on the whole is good. This is understandable since, within a restricted series such as that in Table 5, the successive introduction of further groups or atoms in place of hydrogen will affect the magnitudes of bond moments and force constants only slightly, so that (as Coop and Sutton (1938) pointed out) $_AP$ should in such cases be roughly additive ; and as the additivity of $_EP$ is well known from molecular refractivity, an additivity of the sum $_EP+_AP$ is logically to be expected.

VI. Acknowledgment

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AN INTERFACE REACTION OF HEXAVALENT CHROMIUM: THE POLAROGRAPHIC BEHAVIOUR OF $HCrO_4^-$ AND CrO_4^{2-}

By J. H. Green*† and A. Walkley*

Summary

Current-voltage relationships have been determined for the electroreduction of dilute chromate solutions in a range of bicarbonate-carbonate buffers at the dropping mercury electrode. Double waves are obtained whose relative heights are a function of the pH value. By analogy with the behaviour of pyruvic acid an interface reaction with some proton donor prior to the reduction to the trivalent state is suggested $(CrO_4^{2-}+HB \rightarrow HCrO_4^-+B^-)$. The rate constants for the interface reaction are computed for different donors by the method of Koutecký and Brdička (1947). Adsorption-desorption processes in the region of the electrocapillary zero may account for the shape of the current-voltage curves, and, if so, the explanation based simply on an interface reaction will require modification. The occurrence of interface reactions and of adsorption-desorption processes in other inorganic systems is discussed.

I. INTRODUCTION

The equilibria existing in aqueous solution between the best-known hexavalent chromium species $H_2Cr_2O_7$, H_2CrO_4, $Cr_2O_7^{2-}$, $HCrO_4^-$, CrO_4^{2-} have been studied by several workers with substantial agreement on the constants involved (Sherrill 1907 ; Neuss and Rieman 1934 ; Endrédy 1936 ; Ricci 1952). In the dilute, neutral to alkaline solutions examined here the more acid and more highly condensed species do not occur in significant amounts, so that the composition of such solutions should be determined by the equilibrium

$$HCrO_4^- \rightleftharpoons CrO_4^{2-}+H^+, \quad \dots\dots\dots\dots (1)$$

for which the value $K=3\cdot20\times10^{-7}$, that is, $pK=6\cdot50$, carefully determined by Neuss and Rieman, will be accepted.

Very few precise electrochemical data are available on any of the hexavalent species, in spite of their practical significance in chrome plating, as corrosion inhibitors, organic oxidants, and in some of the newer types of primary cell. Most polarographic studies except those of Lingane and Kolthoff (1940) have dealt with reductions from the trivalent state. These authors found four waves in the current-voltage curves of neutral unbuffered chromate solutions and identified the three most negative as due to 3-, 4-, and 6-electron changes.

The most positive wave, at -0.3 V $v.$ S.C.E., whose height was not proportional to concentration, was thought due to a 3-electron reduction of chromate ion, hindered to such an extent by the formation of a film of chromium hydroxide or chromium chromate, that reduction was only completed at the potential of -1.1 V. The same explanation was offered to account for the behaviour of chromates in several different buffers of pH 10–12. In the present study the electroreduction from Cr^{VI} to Cr^{III} has been conducted using one type of buffer $(CO_2 - HCO_3^- - CO_3^{2-})$ as indifferent electrolyte, covering the pH range 6·5 to 12·5.

II. Materials and Apparatus
(a) Materials

A range of solutions of K_2CrO_4, Na_2CO_3, $NaHCO_3$ was prepared from salts of analytical reagent grade, the concentration of K_2CrO_4 being $4.95 \times 10^{-4}M$ in each. The total molality of the buffer salts was kept at 0·05 in the solutions of pH 9·0 to 11·3, while small additions of NaOH were made to 0·05M Na_2CO_3 to produce the most alkaline solution. The most acid solution was prepared by passing CO_2 through 0·05M $NaHCO_3$, the gas serving also to deaerate the electrolyte.

(b) Apparatus

Most of the current-voltage curves were plotted automatically on a Leeds-Northrup Electrochemograph but some were obtained by manual control. Those shown in Figure 1 have been traced in reverse from the recorder chart in order to conform to the usual polarographic convention.

The cell was of the H pattern, as described by Komyathy, Molloy, and Elving (1952). A sintered glass disk and agar plug separated cathode compartment from the combined working anode-reference electrode, which was a saturated calomel half-element of large surface area. All potentials quoted are negative to this. The capillary characteristics measured at 1·0 V and at pH 11·27 with a head of 40·8 cm Hg were $m=2.86$ mg sec^{-1}, $t=3.18$ sec, $m^{2/3}t^{1/6}=2.44$ mg$^{2/3}$ sec$^{-1/2}$. All measurements were conducted at 25 ± 0.1 °C in an atmosphere of nitrogen or carbon dioxide. A glass electrode placed in the cathode compartment was used to determine the bulk pH value before and after electrolysis, lithium glass being employed for the more alkaline solutions.

All limiting currents were corrected for the appropriate residual currents, and all half-wave potentials were corrected for the small iR drop in the cell ($c.$ 10 mV). Where potentials were obtained from curves plotted automatically an additional small correction is necessary due to the lag in the instrument. The extent of the error found agreed with that found by McKenzie and Taylor (1948).

III. Experimental Results
(a) Variation of Limiting Current with pH Value

The limiting currents obtained at the applied potentials 1·0 and 1·5 V for electrolytes of different pH values are shown in Table 1, and some of the current-voltage curves from which the data were obtained are reproduced in

TABLE 1

LIMITING CURRENTS FOR REDUCTION OF $4\cdot95\times10^{-4}$ M K_2CrO_4 IN BICARBONATE-CARBONATE BUFFERS MEASURED AT TWO DIFFERENT APPLIED VOLTAGES

pH	Limiting Currents (μA)		
	At $1\cdot5$ V	At $1\cdot0$ V	Difference
$6\cdot56$	$8\cdot0$	$8\cdot0$	$0\cdot0$
$6\cdot60$	$7\cdot7$	$7\cdot7$	$0\cdot0$
$8\cdot99$	$7\cdot5$	$5\cdot6$	$1\cdot9$
$9\cdot20$	$7\cdot8$	$5\cdot8$	$2\cdot0$
$9\cdot47$	$7\cdot4$	$4\cdot8$	$2\cdot6$
$9\cdot47$	$7\cdot4$	$4\cdot7$	$2\cdot7$
$10\cdot10$	$7\cdot7$	$3\cdot4$	$4\cdot3$
$11\cdot27$	$7\cdot5$	$1\cdot0$	$6\cdot5$
$12\cdot50$	$7\cdot0$	$0\cdot1$	$6\cdot9$
$12\cdot50$	$6\cdot9$	$0\cdot1$	$6\cdot8$

Figure 1.   Below pH 7 and above pH 12 only one wave is found, but at intermediate pH values two waves are obtained, the second increasing in height at the expense of the first as the pH rises.   The third wave which occurs at $E_{\frac{1}{2}}=1\cdot75$ V is probably due to the reduction of Cr^{III} (or Cr^{VI} via Cr^{III}) to chromium metal.
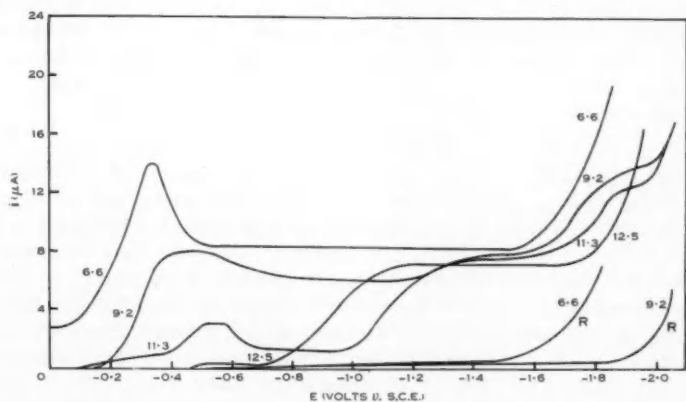
Fig. 1.—Current-voltage curves for $4\cdot95\times10^{-4}$M K_2CrO_4 in bicarbonate-carbonate buffers of pH value shown.* R=residual current.

* Unpublished work by Dr. D. R. Stevenson and Dr. A. Langer (Scientific Paper No. 1022, 1941, Westinghouse Research Laboratories, East Pittsburgh, Penn., U.S.A.), which they have kindly made available to us, shows that a similar family of current-voltage curves is obtained when borate buffers are used as supporting electrolytes.

D

(b) Variation of Limiting Current with Pressure of Mercury at the Dropping Electrode

To decide whether the reduction processes were rate- or diffusion-controlled the current-voltage relationships were redetermined for different heights of the mercury column. The latter have been corrected for the back pressure due to interfacial tension at the drop surface (Table 2).

TABLE 2

VARIATION OF LIMITING CURRENTS WITH PRESSURE OF MERCURY AT DROPPING ELECTRODE.
REDUCTION OF $4 \cdot 95 \times 10^{-4}$M K_2CrO_4 IN BICARBONATE-CARBONATE BUFFER OF pH $11 \cdot 27$

Head of Mercury (cm)	Pressure Correction (cm)	Effective Head of Mercury, h (cm)	Limiting Currents (μA)		$\dfrac{i_d}{h^{\frac{1}{2}}}$
			At $0 \cdot 9$ V i_k	At $1 \cdot 5$ V i_d	
$20 \cdot 0$	$1 \cdot 5$	$18 \cdot 5$	$1 \cdot 0$	$4 \cdot 7$	$1 \cdot 09$
$30 \cdot 0$	$1 \cdot 5$	$28 \cdot 5$	$1 \cdot 1$	$6 \cdot 0$	$1 \cdot 12$
$40 \cdot 8$	$1 \cdot 5$	$39 \cdot 3$	$1 \cdot 0$	$7 \cdot 5$	$1 \cdot 19$
$50 \cdot 0$	$1 \cdot 5$	$48 \cdot 5$	$0 \cdot 8$	$7 \cdot 6$	$1 \cdot 09$
$70 \cdot 0$	$1 \cdot 5$	$68 \cdot 5$	$1 \cdot 0$	$9 \cdot 7$	$1 \cdot 17$

IV. DISCUSSION

(a) An Interface Reaction as the Rate-Controlling Process

Reductions in solutions more acid than pH $6 \cdot 5$, where the process occurs at potentials more positive than that of the S.C.E., are not shown in Figure 1, but the same diffusion current is obtained at pH $4 \cdot 5$ as at $6 \cdot 5$. It therefore seems reasonable to assume that the single step in acid buffers is due to the reduction of $HCrO_4^-$ and the step in strongly alkaline buffers to CrO_4^{2-}. If the reaction

$$CrO_4^{2-} + H^+ \rightarrow HCrO_4^- \quad \ldots\ldots\ldots\ldots\ldots \quad (2)$$

is instantaneous, and if, as seems probable, it is easier to reduce a singly-charged than a doubly-charged negative ion at a negative electrode, only the reduction of the more easily reduced species would be expected even at pH values at which the other greatly predominated. If the reaction time were slow compared to the time required to record a current-voltage curve two waves would be expected whose relative heights were measures of the relative concentrations of the two ions at any one pH value. The way in which the height of the first wave would then decrease is shown by the theoretical dissociation curve (Fig. 2, curve (a)). This may be compared with the experimentally determined curve (b) which shows that the pH at which the first wave has attained half its original height (referred to as pH$_1$) is $9 \cdot 85$ or $3 \cdot 35$ units above the pK value.

The similarity between these results and those for the electroreduction of pyruvic and phenylglyoxylic acids (Brdička 1947) suggests that the displacement of $3 \cdot 35$ units could be due to the production of $HCrO_4^-$ by a very fast reaction between CrO_4^{2-} and some proton donor at the interface. Brdička and Wiesner (1947) have shown that if such an interface reaction is the rate-determining

step, the height of the first wave should be proportional to the surface area of the electrode and therefore independent of the head of mercury, provided a buffer is chosen of such a pH value that the height of the first wave is small compared with that of the second.   On the other hand, the height of the second wave should be proportional to the square root of the head of mercury, as implied by the Ilkovič and Poiseuille equations (diffusion control).   The data of Table 2 show that both these relations hold, and hence that to this extent the behaviour of the organic and inorganic systems is similar.

However, one difference between the two systems is at once apparent. The diffusion current of $HCrO_4^-$ is appreciably greater than that of CrO_4^{2-} whereas the diffusion current for each organic acid is the same as for its respective
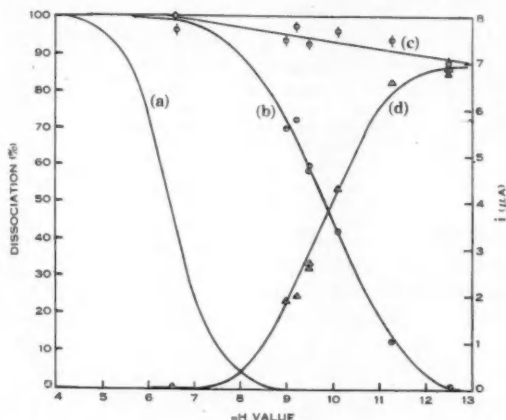
Fig. 2.—Limiting currents for reduction of $4 \cdot 95 \times 10^{-4}M$ K_2CrO_4 in bicarbonate-carbonate buffers. Curve (a) dissociation curve for system $HCrO_4 \rightleftharpoons CrO_4^{2-} + H^+$; curve (b) current measured at $1 \cdot 0$ V ; curve (c) current measured at $1 \cdot 5$ V ; curve (d) difference between currents at $1 \cdot 5$ and $1 \cdot 0$ V.

○ $HCrO_4^-$; △ CrO_4^{2-} ; ⏀ Total Cr.

anion. No independent value of the diffusion coefficient of $HCrO_4^-$ could be found, but the ratio of the diffusion currents observed here for the two ions is what would be expected if the limiting ionic conductances were similar to those of other inorganic acid-base pairs (see Table 3).

(b) The Reaction Rate

The derivation of expressions for the rate of interface reactions has been the subject of several theoretical investigations which have recently been ably reviewed by Gardner and Lyons (1953). The methods of Koutecký and Brdička (1947) and Delahay (1952b), modified by Henke and Hans (1953), give the rate constant k in the form

$$\log k = 2pH - pK - \log t + \log y - \log D_1/D_2, \quad \ldots \ldots (3)$$

where t is the drop time, y is a quantity whose value depends on the ratio of the limiting current for the first reduction process to its maximum value ($i/i_{max.}$), and D_1, D_2 are the diffusion coefficients of $HCrO_4^-$ and CrO_4^{2-}. Taking D_1/D_2 as $1 \cdot 20$ (Table 3), the value of log y corresponding to pH $9 \cdot 85$ as $-0 \cdot 17$ (Henke

TABLE 3

LIMITING IONIC CONDUCTANCES OF ACID-BASE PAIRS AT 25 °C

Ion	Limiting Conductance (cm² sec⁻¹)	Reference	Ratio, $\dfrac{2x}{y}$	Hypothetical Ratio of Diffusion Currents, $\sqrt{\left(\dfrac{2x}{y}\right)}$
HSO_4^- (x) $\frac{1}{2}SO_4^{2-}$ (y)	49·8* 75·7*	Sherrill and Noyes (1926)	1·31	1·14
$H_2PO_4^-$ $\frac{1}{2}HPO_4^{2-}$	36 57	Landolt - Börnstein (1936)	1·26	1·12
HCO_3^- $\frac{1}{2}CO_3^{2-}$	44·5 72	Landolt - Börnstein (1936)	1·24	1·11
$HC_2O_4^-$ $\frac{1}{2}C_2O_4^{2-}$	40·2 74·1	Darken (1941)	1·08	1·04
$HCrO_4^-$ $\frac{1}{2}CrO_4^{2-}$	48† 80	Present paper Kolthoff and Lingane (1952)	1·20	1·09

* For 10^{-4}M solutions.

† Calculated from the Nernst and Ilkovič equations, using the data of the present paper.

and Hans 1953), and the appropriate value of the dissociation constant from Neuss and Rieman's (1934) experimentally determined relation

$$pK_{CrO_4^{2-}} = 6 \cdot 50 - \frac{1 \cdot 5\sqrt{I}}{1 + 0 \cdot 7\sqrt{I}}, \qquad \dots \dots \dots \dots \dots \text{(4)}$$

where I is the ionic strength, expression (3) can be evaluated as

$$\log k = 19 \cdot 70 - 6 \cdot 08 - 0 \cdot 50 - 0 \cdot 17 - 0 \cdot 08$$
$$= 12 \cdot 87,$$
$$k = 7 \cdot 4 \times 10^{12} \text{ l. mol}^{-1} \text{ sec}^{-1}.$$

It is at once pertinent to ask whether such a result is compatible with that calculated from collision theory. Debye's (1942) method assumes that every collision is effective, and that diffusion modified by the effect of the electrostatic field is the rate-controlling step. The rate constant is given by

$$k = \frac{4\pi z^+ z^- e^2 N}{1000\varepsilon k_B T} \cdot \frac{D^+ + D^-}{\exp(z^+ z^- e^2/\varepsilon a k_B T) - 1}, \qquad \dots \dots \dots \text{(5)}$$

where z^+, z^-, D^+, D^- are the number of charges and the diffusion coefficients of the ions whose closest distance of approach is a, ε is the dielectric constant, e the electronic charge, N Avogadro's number, k_B the Boltzmann constant, and T the absolute temperature. Taking the macroscopic value $78 \cdot 5$ for ε, 4 angstrom units for a, and Kolthoff and Lingane's (1952) values for the diffusion coefficients of H^+ and CrO_4^{2-}, k proves to be 1×10^{11} l. mol^{-1} sec^{-1}. One of the few fast reaction rates so far determined is that of the structurally similar sulphate ion with a hydrogen ion, namely, $SO_4^{2-} + H^+ \rightarrow HSO_4^-$. From ultrasonic absorption measurements in H_2SO_4 solution Eigen, Kurtze, and Tamm (1953) find $k = 10^{11}$ l. mol^{-1} sec^{-1}.

For pyruvic and phenylglyoxylic acids ($pH_{\frac{1}{2}} = 6 \cdot 2$ and $6 \cdot 8$ resp.) it appears that reaction occurs almost solely with hydrogen ions, whereas in the chromate system, with $pH_{\frac{1}{2}}$ three units higher, the hydrogen ion might be expected to play a relatively smaller part. The three possible ways for the chromate ion to take up a proton can be written as

$$CrO_4^{2-} + H^+ \rightarrow HCrO_4^-, \quad \dots\dots\dots\dots\dots (6)$$
$$CrO_4^{2-} + HCO_3^- \rightarrow HCrO_4^- + CO_3^{2-}, \quad \dots\dots\dots (7)$$
$$CrO_4^{2-} + H_2O \rightarrow HCrO_4^- + OH^-. \quad \dots\dots\dots (8)$$
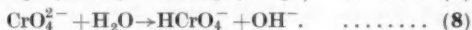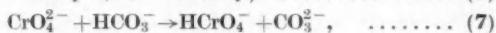
In deriving equation (3) Koutecký and Brdička assumed that the hydronium ion was the sole proton donor but their procedure can be readily adapted to the case where the buffer acid is the sole donor. This yields an equation similar to (3) except for the addition of two extra terms, namely,

$$\log k = 12 \cdot 87 - \log m + \log ([H^+] + K_{CO_3^{2-}}), \quad \dots\dots\dots (9)$$

where $m = [HCO_3^-] + [CO_3^{2-}]$ and $K_{CO_3^{2-}}$ is the second dissociation constant of carbonic acid. Using the experimentally determined relation of Harned and Scholes (1941) and MacInnes and Belcher (1933),

$$pK_{CO_3^{2-}} = 10 \cdot 33 - 0 \cdot 382 \sqrt{I},$$

the rate equation is then evaluated as

$$\log k = 12 \cdot 87 + 1 \cdot 30 + \log (10^{-9 \cdot 85} + 10^{-10 \cdot 20})$$
$$= 4 \cdot 47,$$
$$k = 3 \cdot 0 \times 10^4 \text{ l. mol}^{-1} \text{ sec}^{-1}.$$

As might be expected an even smaller value of k is obtained if water is assumed to be the sole donor.

The results obtained when the buffer strength is increased lend support to the view that the bicarbonate ion is the chief donor. When m is increased tenfold the first limiting current increases at the expense of the second at any one pH value. Equation (9) predicts such an increase in $pH_{\frac{1}{2}}$ for an increase in m when k is constant; and in addition an increase in k might be expected, due to the salt effect in a reaction between two negative ions, one of them doubly charged. If the interface reaction were predominantly one between CrO_4^{2-} and H^+ the rate constant would be independent of m (eqn. (3)) and any

primary salt effect would be negative. Hence the observed increase in $pH_{\frac{1}{2}}$ would have to be explained as an improvement in buffering, and the new rate constant would be higher than that already shown to exceed the value calculated by the Debye equation. The buffering appears to be adequate. Thus the $pH_{\frac{1}{2}}$ value lies within the maximum range $(10 \cdot 3 \pm 1$ units) of the $HCO_3^- - CO_3^{2-}$ system, and a calculation along similar lines to that suggested by Delahay (1952a) shows that with the small current density of 2×10^{-4} A/cm² used, the $[H^+]$ in the reaction layer is decreased by only about 1 per cent. in the presence of the $0 \cdot 05M$ buffer.

(c) An Alternative Explanation

A modification of the above interpretation is suggested by the work of Kriukova (1949) who found that after the normal diffusion plateau had been reached in the reduction of the persulphate anion the current fell rapidly to low values and subsequently rose again at a much more negative potential. She suggested that $S_2O_8^{2-}$, adsorbed on the mercury at potentials more positive than the electrocapillary zero, was so strongly repelled when the surface became negatively charged that the number of ions reaching the surface was considerably reduced. Neutral unbuffered electrolytes were used and a change in pH did not alter the current-voltage curve. Somewhat similar behaviour has been shown for $PtCl_4^{2-}$ (Laitinen and Onstott 1950a), $Fe(CN)_6^{3-}$ (Frumkin and Florianovich 1951), and $S_4O_6^{2-}$ (Zezula 1953). Reduction of these and of $S_2O_8^{2-}$ begins close to zero voltage (v. S.C.E.) as does that of $HCrO_4^-$, but unlike the reduction of the first four the last involves a hydrogen ion, so that its $E_{\frac{1}{2}}$ value becomes more negative with increasing pH value, passing through the electrocapillary zero* at about pH 11. This transfer of the potential region of reduction to one where repulsion is strong might account for the diminution of current with pH increase.

It should be noted that all the early work on reduction of anions (see Heyrovsky 1941; Kolthoff and Lingane 1952) relates to the singly-charged ions NO_3^-, IO_3^-, BrO_3^-, where the difficulty of reduction is shown by a high overvoltage which can be reduced if the negative field is screened by polyvalent cations. Neither these nor the singly-charged organic ions pyruvate, phenyl-glyoxylate, azobenzene-p-carboxylate (Rüetschi and Trümpler 1952) show the type of maxima seen in Figure 1. The $HCrO_4^- - CrO_4^{2-}$ system differs from others previously studied in having a doubly-charged ion which requires proton for its reduction, and which can accept a proton to form its corresponding acid, the latter being reduced in the region of the electrocapillary zero. The sharp maximum observed at pH $6 \cdot 5$ is suppressible by gelatin but the rounded peaks at higher pH values are not. Moreover, the current responsible for these peaks never exceeds the diffusion current for the reduction of $HCrO_4^-$.

In the reduction of $S_2O_8^{2-}$, $PtCl_4^{2-}$, $Fe(CN)_6^{3-}$, and $S_4O_6^{2-}$ it was shown that increasing the indifferent electrolyte concentration increased the minimum current flowing, in some instances removing the minimum altogether. In our

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* Grahame (1947) gives $-0 \cdot 45$ V v. S.C.E. for mercury in $0 \cdot 5M$ K_2CO_3.

system a tenfold increase in concentration of buffer of pH 10·4 only raised the minimum current (plateau current at potential—1·0 V) from 2·9 to 4·0 µA, and the peak current (at −0·6 V) not at all. It therefore seems probable that the peak values for each alkaline solution represent the maximum obtainable at that pH, the screening by the buffer cations in 0·5M concentration being adequate. Reduction may be expected to occur via the less strongly repelled $HCrO_4^-$ so that the same explanation of a preprotonation of CrO_4^{2-} holds as before, except that peak values rather than minima should be plotted in curve (b), Figure 2. This curve would be moved to the right by about 1 unit and rate constants calculated from it would be about a hundredfold higher.

The differences between the two interpretations can be summarized as follows. The first regards the peaks as maxima of a type not suppressible with the usual reagents, and the subsequent plateau currents as the true limiting currents. Increase of current with increase of buffer strength is explained as a salt effect and as an increase in the concentration of the reacting species HCO_3^-. We have assumed, as others have done in this field, that the pH in the reaction layer does not differ significantly from that in the bulk. The second interpretation gives a plausible explanation of the origin of the peaks and regards the subsequent plateaux as minima whose heights depend largely on the cation screening. The adsorption-desorption theory does not explain the big individual differences between various anions recorded by Frumkin and Florianovich.

Further experiments with electrolytes of varying buffer capacity, ionic strength, and ionic charge should remove many of the present uncertainties. There seems no reason why the unusual behaviour of the chromate ion should be peculiar to the mercury electrode or even to electroreductions. Westheimer (1949) considers that $HCrO_4^-$ and not $Cr_2O_7^{2-}$ is the active species in the oxidation of many organic substances. Similarly, in studying the surface reactions of steel in chromate solutions, Powers and Hackerman (1953) found that the amount of adsorbed chromium followed the $HCrO_4^-$ content rather than that of any other species present. Again, the failure to reduce $Cr_2O_7^{2-}$ even at very negative applied potentials at a rotating platinum electrode is reported by Kolthoff and Lingane (1952).

(d) Other Possible Interface Reactions in Inorganic Systems

There have been many reported cases of " pre-waves " in the current-voltage curves of cations thought to be due to two species in hydrolytic equilibrium, for example, $Co(H_2O)_5OH^+$ and $Co(H_2O)_6^{2+}$; $VOOH^+$ and VO^{2+} ; UO_2OH^+ and UO_2^{2+}, but it is of interest to note that wherever there is a clear case of doublet waves with a pH dependence the reacting species are anions.

Some examples follow :

(i) Selenious Acid.—The acid-base pairs H_2SeO_3-$HSeO_3^-$ and $HSeO_3^-$-SeO_3^{2-}, with pK values of approximately 3 and 8 respectively, show limiting currents with a strong pH dependence, but the picture is complicated by a reduction producing mercuric selenide (Lingane and Niedrach 1949).

(ii) *Sulphites.*—Foffani and Dall'Aglio (1952) have shown that in buffered solutions of sulphite the limiting current for the first reduction decreases with increasing pH, suggesting a process limited by the rate of the interface reaction

$$HSO_3^- + H^+ \rightarrow H_2SO_3 \qquad pK = 1 \cdot 76.$$
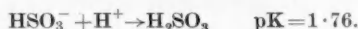
The $pH_{\frac{1}{2}}$ value is $5 \cdot 0$.

(iii) *Tetravalent Ruthenium.*—Niedrach and Tevebaugh (1951) have shown a strong pH dependence for the first two limiting currents observed in the reduction of ruthenium from the $+4$ to the $+3$ state in perchloric acid. The $pH_{\frac{1}{2}}$ value seems to occur in solutions of about $0 \cdot 3M$ $HClO_4$.

(iv) *Polytungstates and Polymolybdates.*—No very close parallel can be expected between the behaviour of CrO_4^{2-}, MoO_4^{2-}, and WO_4^{2-}. The two latter ions are not reducible polarographically and a fairly low pH value must be attained before any $+6$ Mo or W species can be reduced. In solutions of $+6$ Mo buffered at pH $2 \cdot 8$, Boltz, de Vries, and Mellon (1949) found a double wave whose pH-dependence should be worth investigating more closely. Some of Souchay's (1952) current-voltage curves for the phospho-9-tungstates show doublet waves.

(v) *Periodates.*—The current voltage curves of Souchay (1948) in carbonate buffers show similarities to those of chromates and the equilibrium

$$H_3IO_6^{2-} + H^+ \rightleftharpoons H_4IO_6^- \qquad pK = 6,$$

may be involved. The curves have strongly developed maxima and minima, the current fall occurring well on the positive side of the usual value of the electrocapillary maximum.

(vi) *Pyrophosphate Complexes of Copper.*—A strong pH-dependence is shown in current-voltage curves with pronounced rounded maxima and minima. The reacting species are thought to be $CuP_2O_7^{2-}$ and $HCuP_2O_7^-$ (Eriksson 1949). or possibly other species with still higher charge (Laitinen and Onstott 1950b).

V. Acknowledgments

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LIQUID–VAPOUR EQUILIBRIA

VI. THE SYSTEMS ACETONITRILE + BENZENE AT 45 °C AND ACETONITRILE + NITROMETHANE AT 60 °C

By I. Brown* and F. Smith*

Summary

Liquid-vapour equilibrium data are given for the systems acetonitrile + benzene at 45·00 °C and acetonitrile + nitromethane at 60·00 °C. These data are used to calculate the excess free energy of mixing for these systems.

I. Introduction

The liquid-vapour equilibrium data for these systems have not been recorded in the literature. The present measurements were made to provide isothermal values of the excess free energy of mixing required for an investigation of the thermodynamic properties of solutions of polar liquids.

II. Experimental

(a) Apparatus

The liquid-vapour equilibrium and vapour pressure measurements were made by the methods used by Brown and Smith (1954a). The acetonitrile + benzene system was analysed by refractive index measurements using a Hilger-Chance precision refractometer maintained at $25\cdot00\pm0\cdot01$ °C. The acetonitrile + nitromethane system was analysed by density measurements as used by Brown and Ewald (1950).

(b) Purification and Properties of Components

The acetonitrile was purified by the method used by Brown and Smith (1954b) and the benzene by the method of Brown and Ewald (1951). The nitromethane was purified by careful fractional distillation through a column 76 cm long, 13 mm in diameter, packed with 1·6 mm Dixon packing, and operated at a reflux ratio of 10 : 1 at a head pressure of 104 mm Hg. The middle fractions boiling at a constant temperature ($\pm0\cdot01$ °C) and having a constant density were retained and used immediately. The physical properties of the components are shown in Table 1.

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TABLE 1

PHYSICAL PROPERTIES OF COMPONENTS

Property				Acetonitrile	Benzene	Nitromethane
B.p./760 mm Hg (°C) ..	..	..		81·57	80·07	101·07
$d_4^{25\cdot00}$ ..	..	..	..	0·77656	0·87369	1·13107
$n_D^{25\cdot00}$ ..	..	..	..	1·34154	1·49803	1·37971
Vapour pressure						
45·00 °C ..	..	..	..	208·35	223·66	—
60·00 °C ..	..	..	..	368·00	—	178·18

The vapour pressure of nitromethane was measured using the equilibrium still and the data are given in Table 2. These data were fitted by the method of Willingham *et al.* (1945) to the Antoine equation

$$\log_{10} P = A - \frac{B}{c+t},$$

where P is in standard mm Hg and t in °C. The values of the constants found and the standard deviation σ of the fit are given in Table 2.

TABLE 2

THE VAPOUR PRESSURE OF NITROMETHANE

t (°C)	P (mm Hg)	Antoine Equation Constants
101·36	767·09	
101·04	759·63	
100·30	742·34	$A = 7\cdot15311$
95·85	645·36	$B = 1365\cdot312$
89·34	522·24	$C = 218\cdot508$
83·96	435·50	$\sigma = 0\cdot16$ mm Hg
74·31	309·37	
64·33	211·86	
60·55	182·25	
55·00	144·83	
49·88	116·38	

Recent vapour pressure measurements by McCullough *et al.* (1954) gave 101·19 °C for the normal boiling point of nitromethane and a pressure of 178·06 mm Hg at 60·00 °C compared with our values of 101·07 °C and 178·18 mm Hg.

(c) Analytical Methods

The liquid and vapour samples from the system acetonitrile+benzene were analysed by refractive index measurements. The refractive index-composition data obtained on mixtures prepared by weighing are given in Table 3. The method of Brown and Smith (1954a) was employed to calculate

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the composition using equation (1) and a graph of the residuals Δ plotted against refractive index. Values of the residual were given by

$$\Delta = n - n_1 - x_2(n_1 - n_2) + 3 \cdot 087(n - n_1)(n - n_2), \quad \ldots \ldots (1)$$

where x_1 is the mole fraction of acetonitrile, x_2 is the mole fraction of benzene and n, n_1, and n_2 are the refractive indices of the mixture, pure acetonitrile and pure benzene respectively.

TABLE 3

ACETONITRILE + BENZENE

Refractive index-composition data

x_1	$n_D^{25 \cdot 00}$	Δ
0·0604	1·49233	+0·00111
0·1005	1·48826	+0·00154
0·1998	1·47758	+0·00223
0·3050	1·46506	+0·00219
0·4011	1·45244	+0·00157
0·5070	1·43721	+0·00056
0·5130	1·43635	+0·00055
0·5959	1·42316	—0·00047
0·7038	1·40446	—0·00159
0·8059	1·38490	—0·00215
0·8992	1·36510	—0·00188
0·9493	1·35366	—0·00121

The samples from the system acetonitrile + nitromethane were analysed by density measurements. The density-composition data obtained on mixtures

TABLE 4

ACETONITRILE + NITROMETHANE

Density-composition data

x_1	$d_4^{25 \cdot 00}$	Δ'
0·0572	1·11163	+0·00003
0·1051	1·09527	+0·00007
0·2058	1·06070	+0·00014
0·3055	1·02612	+0·00013
0·4018	0·99237	+0·00007
0·5010	0·95730	—0·00003
0·5068	0·95523	—0·00002
0·5578	0·93708	—0·00006
0·5948	0·92389	—0·00007
0·6985	0·88668	—0·00009
0·7996	0·85000	—0·00013
0·8391	0·83562	—0·00011
0·9033	0·81212	—0·00013
0·9459	0·79651	—0·00007

prepared by weighing are given in Table 4. The method of Brown and Smith (1954b) was employed to calculate the composition using equation (2) and a

graph of the residuals Δ' plotted against density. Values of the residual for the system were given by

$$\Delta' = d - d_2 + x_1(d_2 - d_1) + 0 \cdot 1229(d - d_1)(d - d_2), \quad \ldots \ldots \ (2)$$

where x_1 is the mole fraction of acetonitrile and d, d_1, and d_2 are the densities of the mixture, pure acetonitrile and pure nitromethane respectively.

III. Liquid-Vapour Equilibrium Data

The liquid-vapour equilibrium data are shown in Tables 5 and 6, where x_1 and y_1 are the mole fractions of acetonitrile in the liquid and vapour respectively, P is the total pressure in standard mm Hg, and α is the relative volatility given by $\alpha = y_1 x_2 / y_2 x_1$.

TABLE 5

ACETONITRILE + BENZENE AT 45·00 °C

Experimental data and derived functions

x_1	y_1	P	α	μ_1^E	μ_2^E	G_x^E
0·0455	0·1056	239·70	2·477	637·1	2·3	31·4
0·0940	0·1818	251·67	2·142	548·4	9·9	60·5
0·1829	0·2783	264·66	1·723	423·4	28·4	100·6
0·2909	0·3607	273·45	1·376	310·5	63·3	135·2
0·3980	0·4274	277·49	1·129	226·0	107·9	154·9
0·5069	0·4885	278·03	0·9294	156·8	165·6	161·1
0·5458	0·5098	277·36	0·8658	134·9	189·8	159·8
0·5946	0·5375	275·86	0·7924	110·2	222·3	155·6
0·7206	0·6157	268·46	0·6211	56·3	326·1	131·7
0·8145	0·6913	257·81	0·5099	26·5	423·7	100·2
0·8972	0·7869	242·50	0·4230	9·3	527·5	62·6
0·9573	0·8916	225·30	0·3668	2·3	612·9	28·4

TABLE 6

ACETONITRILE + NITROMETHANE AT 60·00 °C

Experimental data and derived functions

x_1	y_1	P	α	μ_1^E	μ_2^E	G_x^E
0·0951	0·1741	195·50	2·006	+0·3	−0·4	−0·3
0·1940	0·3255	213·70	2·005	+0·5	−0·4	−0·2
0·2930	0·4539	232·24	2·006	−0·2	+0·2	+0·1
0·3939	0·5658	251·20	2·005	−0·4	+0·7	+0·3
0·4614	0·6325	264·24	2·009	+0·8	+0·8	+0·8
0·5001	0·6674	271·45	2·006	+0·1	+1·5	+0·8
0·6051	0·7548	291·64	2·009	+0·7	+1·6	+1·0
0·8055	0·8925	329·97	2·005	−0·2	+3·2	+0·5
0·9025	0·9488	349·17	2·002	+0·4	+5·1	+0·9
0·9486	0·9737	358·27	2·006	+0·6	+4·2	+0·8

These data show that an azeotrope is formed at 45·00 °C having a mole fraction of 0·457 acetonitrile at a total pressure of 278·1 mm Hg.

IV. DERIVED THERMODYNAMIC FUNCTIONS

The excess chemical potentials μ_1^E and μ_2^E and the excess free energy of mixing G_x^E were calculated from the equilibrium data using equations (2), (3), and (4) of Brown and Smith (1954a). The values obtained (cal/g-mol) are shown in Tables 5 and 6.

The values of the liquid molar volumes V_1 and V_2 and the second virial coefficient in the equation of state for the mixed vapours, β_{12}, were obtained by the methods given by Brown and Smith (1954a).

Values of the second virial coefficient for acetonitrile β_{11} were obtained by extrapolation from the experimental values of Lambert et al. (1949). The values for benzene were obtained from the equation given by Allen, Everett, and Penney (1952) and the values for nitromethane from the equation given by Douslin (1954) which is based on the experimental data of McCullough (1954).

The values of the second virial coefficients and molar volumes (l/mol) used for the system acetonitrile+benzene at 45 °C were :

β_{11}	β_{22}	β_{12}	δ_{12}	V_1	V_2
$-4 \cdot 500$	$-1 \cdot 236$	$-1 \cdot 173$	$+3 \cdot 39$	$0 \cdot 053$	$0 \cdot 092$

For the system acetonitrile+nitromethane δ_{12} was assumed to be zero as the system is substantially ideal. The values used for this system at $60 \cdot 00$ °C were :

β_{11}	β_{22}	V_1	V_2
$-3 \cdot 350$	$-2 \cdot 500$	$0 \cdot 056$	$0 \cdot 056$

V. DISCUSSION

For the system acetonitrile+benzene at $45 \cdot 00$ °C the excess free energy data were fitted by the method of least squares to equation (3).

$$G_x^E = x_1 x_2 [a + b(x_1 - x_2) + c(x_1 - x_2)^2]. \qquad \ldots \ldots \ldots \text{ (3)}$$

The values (cal/g-mol) of the constants and the standard deviation of the fit σ were :

a	b	c	σ
$+643 \cdot 3$	$-8 \cdot 1$	$+70 \cdot 1$	$0 \cdot 53$

These values do not indicate separation into two liquid phases. The thermodynamic consistency of the results was tested by the method used previously, the ratio of areas above and below datum in a plot of $\mu_1^E - \mu_2^E$ against x_1 was $1 \cdot 006$.

The error in G_x^E due to errors in the directly measured quantities was estimated to be of the order of $2 \cdot 5$ cal/mole.

For the system acetonitrile+nitromethane the errors in G_x^E were estimated to be just less than 2 cal/g-mol. The data given in Table 6 show that the excess free energy of mixing is zero within the experimental error over the whole concentration range when the deviations of the vapours from ideal gas behaviour

are allowed for. At 60·00 °C the relative volatility of this system was found to be 2·006 over the whole concentration range.

The excess entropy for these systems will be calculated when heats of mixing have been measured.

VI. Acknowledgment

The authors thank Mr. O. H. Rigby for his help in the purification of the components.

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THE QUINONE–HYDROQUINONE CHARACTER OF ACTIVATED CARBON AND CARBON BLACK

By V. A. Garten* and D. E. Weiss*

Summary

There are two extreme types of activated carbon and carbon black although structures intermediate between these two extremes are more usual. This work has established that in one extreme, the oxidized form (" H " carbon), the carbon has a pronounced quinonoid structure which creates a number of fixed olefinic bonds. In the other, the reduced form (" L " carbon), the structure is more aromatic and has the characteristics of a hydroquinone. Carbons having properties intermediate between those of a pure " H " or " L " carbon acquire some semiquinone characteristics and become less diamagnetic. It is experimentally shown that the chemical behaviour of these carbons parallels in many ways that of simple quinone-hydroquinone compounds. The quinonoid structure of an " H " carbon accounts for the formation of peroxygen complexes, its ability to catalyse the ionization of oxygen in the presence of an electron donor, its oxidizing properties and its reactivity with rubber. The hydroquinone character of an " L " carbon is responsible for its ability to adsorb alkali, its reducing properties, and its ability to fog a photographic plate (" Russell effect "). The change in properties which occurs in chars carbonized above 650° C is due to the transition from an " L " to an " H " carbon.

I. Introduction

Despite the profusion of literature, which has been reviewed by Steenberg (1944) and Hassler (1951), existing knowledge of the chemical structure of activated carbon and carbon black is far from complete as little of the work has been done with well-defined substances. However, Riley (1939) and co-workers have made extensive X-ray studies of cokes and chars and have concluded that there are present in chars prepared above 400 °C flat aromatic or layer planes which are stacked parallel to each other in threes or fours to form minute crystallites. We shall consider the chemical structure of these crystallites. Although numerous theories have been offered to explain the chemistry of these materials, none is completely satisfactory.

New experimental results are presented which show that activated carbons and carbon blacks are of two types. In one, the oxidized form, the carbon acquires a quinonoid structure which creates a number of fixed olefinic bonds ; in the other, the carbon is reduced and acquires the aromatic structure character-istic of a hydroquinone. This concept has not hitherto been proposed. The established facts concerning the chemistry of activated carbon and carbon black will be summarized, new experiments will then be described to establish this

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concept and the essential similarity of carbon blacks and activated carbon, and finally, the available data will be examined from this point of view. It will be shown from a consideration of the established chemistry of simple quinones and hydroquinones that the new concept satisfactorily provides a consistent explanation for the adsorption of acid and alkali by carbon black and activated carbon, the " reinforcement " of rubber by carbon black, the production of hydrogen peroxide by these carbons, chemisorption, and the change in properties which occurs in chars carbonized above 700 °C. This concept satisfactorily explains the complex chemical behaviour of these carbons on the basis of established reactions in organic chemistry. It is not necessary to postulate the existence of special unsaturated surface carbon atoms (i.e. trivalent carbon) as has been done frequently in the past. Many of the details concern chemical reactions which are so complex that their mechanisms have not yet been elucidated in simpler systems. For this reason the quantitative aspects of the problem will not be considered. Because the accessibility of the surface of pores to chemical reagents may differ considerably in various activated carbons it is difficult to compare the quantitative behaviour of their surface groups. For this reason only qualitative conclusions can be drawn from major differences in the chemical behaviour of the various carbons. The behaviour only of carbons substantially free of nitrogen (less than $0 \cdot 2$ per cent.) and ash (less than $1 \cdot 5$ per cent.) will be considered in detail.

II. REVIEW OF THE LITERATURE

The following facts have been established concerning the chemistry of activated carbon and carbon black and are pertinent to the subsequent discussion.

(a) Crystalline Structure

Riley (1939) has shown that chars prepared from carbohydrates are composed of crystallites having a graphitic structure the size of which increases with the temperature of carbonization. The mechanical strength and electrical conductivity of a char increase rapidly when prepared above 700 °C, at which temperature the char undergoes profound changes.

(b) Activation Temperature

Steenberg (1944) confirmed the earlier findings of Kolthoff (1932) and King (1937) that sugar char activated in moist air at temperatures between 400 and 800 °C adsorbs acid and alkali differently according to the temperature of preparation. When activated at the lower temperatures the carbon adsorbs alkali but only a little acid and was defined by Steenberg as an "L" carbon, whereas that activated at 800 °C and cooled in the absence of air, adsorbs acid but no alkali and was termed an " H " carbon. The pH of a suspension of the carbon in water is greater the higher the temperature of activation. A similar behaviour was observed by Wiegand (1937) when carbon blacks were heated in a vacuum to various temperatures.

(c) Surface Oxides

An acidic oxygen group on the carbon surface is responsible for the adsorption of alkali (Steenberg 1944). The work of Burstein and Frumkin (1929), Schilow

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and Tschmutow (1930a, 1930b), and Bretschneider (1932) has established that
at least another oxide exists whose presence accounts for the adsorption of acid
by the carbon in some unknown way.

(d) Chemical Structure

Villars (1948) studied the reactivity of carbon blacks towards the Grignard
reagent and established the presence of carbonyl oxygen, hydroxyl oxygen, and
a considerable amount of inert ether oxygen. Stearns and Johnson (1951)
obtained evidence of an olefinic structure in carbon black which they suggested
played a role in rubber reinforcement. The degree of unsaturation increased
when the carbon black was calcined.

(e) Peroxides

Russell observed that various coals could fog a photographic plate when
exposed to air and ascribed the effect to the formation of hydrogen peroxide.
The subject has been reviewed by Yohe (1950).

Kolthoff (1932) and King (1933) extracted a peroxide from an " H " carbon
with acid after exposure to moist air. " L " carbons similarly treated yielded
much less peroxide.

(f) The Reducing and Oxidizing Properties of Carbons

Heyman, Salomon, and Kieffer (1930) observed that various activated
carbons could reduce silver, gold, mercuric, and ferric salts. " L " carbons
readily reduce silver nitrate (Bolam and Phillips 1935). On the other hand
some carbons have pronounced oxidizing properties and can, for example,
readily oxidize ferrous iron (Winslow 1947).

(g) Chemisorption

Oxygen, chlorine, bromine, nitric oxide, and nitrous oxide are readily
chemisorbed by carbon. The subject has been reviewed by McBain (1931).

(h) Magnetic Measurements

Wynne-Jones and Blayden (1952) found various chars to be diamagnetic
and that carbon blacks were the least diamagnetic. Honda and Ouchi (1953)
measured the diamagnetic susceptibility of various chars prepared by
carbonizing glucose or cellulose over the temperature range 400–2000 °C. The
diamagnetism was a minimum for the chars activated in the region of 700 °C.
Similar results were found on examining a variety of coals.

III. THEORIES ON ADSORPTION OF ELECTROLYTES BY CARBON

Numerous theories have been proposed to account for the adsorption of
electrolytes by activated carbon and the change in pH which usually occurs
(" hydrolytic " adsorption). These have been critically reviewed by Steenberg
(1944) and also by Hassler (1951). The more recent theories are as follows.

(a) Electrochemical Theory

According to Frumkin (1930) and his co-workers carbons suspended in
solutions of electrolytes function as reversible gas electrodes. The concentration

of ions in the solution and the nature and the pressure of the gas, which is in equilibrium with the system, determined the charge of the carbon. The carbon is believed to become negatively charged when in contact with hydrogen due to ionization of adsorbed hydrogen atoms. It behaves similarly to a platinum-hydrogen electrode. In the presence of alkali the liberated hydrogen ions are neutralized and the alkali cations are supposed to be attracted to the negatively charged carbon surface, thus causing adsorption. In the presence of oxygen, hydroxyl ions are produced and the carbon is supposed to acquire a positive charge which results in the adsorption of anions. This theory does not agree with the facts that a completely outgassed carbon can adsorb electrolytes, that carbon does not behave as a reversible hydrogen electrode, and that no exponential relation has been observed between the gas pressure of the system and the adsorption of electrolytes.

(b) Steenberg's Theory

Steenberg (1944) has proposed the most satisfactory theory to date to account for the adsorption of electrolytes by activated carbon. According to him alkali is neutralized by acidic groups on an " L " carbon surface which functions as a cationic exchange adsorbent. Acid is not adsorbed by ion exchange with an " H " carbon since its adsorption is inhibited by non-electrolytes. Its adsorption is due to " primary " adsorption of a hydrogen ion by short range adsorption forces and " secondary " adsorption of a chloride counter-ion. Similarly, an organic ion can be primarily adsorbed and its counter-ion secondarily adsorbed. Competitive exchange of the latter with the hydrogen or hydroxyl ions of water accounts for the pH change which accompanies the adsorption.

IV. SUMMARY OF THE PROBLEM

There is in the literature no single concept that can reconcile all the facts summarized in Section II. Thus Steenberg's conception clearly explains the pH changes which accompany the adsorption of organic electrolytes, but fails to explain why the adsorption of acid by an " H " carbon is related to oxygen complexes on the carbon. It makes no attempt to explain the reducing character of an " L " carbon, the oxidizing properties of some carbons, the formation of peroxides which may be extracted with acids from " H " carbons, and the change in magnetic susceptibility with the temperature of activation.

No attempt has ever been made to relate the behaviour of activated carbons and carbon blacks ; nor does any chemical basis exist to explain the reinforcement of rubber by carbon black. Before all the well-established facts can be reconciled into a single concept further experimental results are required with defined materials. The following experiments were performed with this in mind.

V. EXPERIMENTAL

A series of activated carbons was made from sucrose by air activation at temperatures between 400 and 800 °C. These were characterized as fully as possible by determining their ability to adsorb acid and alkali, the pH value of

their suspension in boiled water,* their ultimate analysis, their ash and iron content, and their surface area. The chemical behaviour of an " H " carbon when reduced by electrochemical methods was studied. The acidity of the acidic groups of an " L " carbon was investigated potentiometrically. The ability of the carbon to reduce silver nitrate was measured. The irreversible adsorption of iodine by the carbons was determined. Magnetic measurements were made on some carbons that had been carefully purified to reduce their ash content to a minimum. A short investigation was also made of the properties of a chlorinated " L " carbon.

(a) Techniques

The experimental methods adopted are as follows :

(i) *Preparation of the Carbon.*—The activated carbons were made according to the method of King (1937) and Steenberg (1944) from charred sucrose. The chars were activated for 13 hr in a slow stream of moist air followed by treatment in a stream of dry air for 1 hr. They were then cooled in a stream of nitrogen. The nitrogen was stripped of oxygen by passing it over copper at 400 °C which had previously been reduced with hydrogen. The carbons were stored under nitrogen to minimize oxidation. Four chars were prepared at temperatures of 400, 550, 650, and 800 °C respectively. They will be given the code numbers C^1_{400}, C^1_{550}, C^1_{650}, and C^1_{800}. Three further lots of chars were made by the same technique at 400 and 800 °C and although similar qualitatively to the previous batches they differed quantitatively. They will be given the code numbers C^3_{400}, C^3_{800}, C^4_{400}, C^4_{800}, and C^5_{400}. The following commercial carbon blacks were used :

" Kosmos 20 "† (semi-reinforcing furnace black),
" Kosmos HM "† (medium processing channel black),
" Spheron 3 "‡ (hard processing channel black),
" Black Pearl 2 "‡ (pelletized pigment black).

Magnetic measurements were made on a special series of low ash carbons prepared as follows : A.R. sucrose was charred and ground to pass a 32 mesh British Standard screen. The char was then boiled with 6N hydrochloric acid and after filtering boiled again with dilute hydrochloric acid and again filtered. This removed a considerable amount of iron. Digestion with 45 per cent. hydrofluoric acid on a water-bath followed by a similar treatment with concentrated hydrochloric acid was repeated twice in order to break up siliceous iron and other silicates. Silica was driven off as the fluoride by evaporation to dryness. The char was subsequently boiled with 6N hydrochloric acid and then with dilute hydrochloric acid to remove any liberated iron or other elements. It was then washed several times and extracted in a Soxhlet extractor with 0·1N acetic acid for 4 days, after which time no further chloride could be detected in the washings. The acetic acid prevented hydrolysis of the ferric

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* This procedure has been widely adopted to classify carbon blacks (Wiegand 1937).

† Products of the United Carbon Co., Ind., U.S.A.

‡ Products of Godfrey L. Cabot Inc., U.S.A.

chloride. The char was finally extracted with water for 2 days to remove the acetic acid and then dried for 8 hr at 90 °C. It was then activated as above at 400, 550, 650, and 800 °C. These carbons are designated as C_{400}^2, C_{550}^2, C_{650}^2, and C_{800}^2 respectively.

(ii) *Preparation of the Chlorinated Carbon.*—" L " carbon C_{400}^3 was heated in a stream of chlorine for 7 hr at 400 °C and then cooled in a stream of nitrogen freed of oxygen. Copious amounts of hydrochloric acid were evolved during the chlorination. It was washed with water for 3 days to free it of physically adsorbed chlorine. Chlorine could not be detected in the wash water after this time.

(iii) *Sodium Hydroxide Adsorption.*—Following Steenberg, $1 \cdot 000$ g of carbon was added to 10 ml of water and allowed to stand for 2 hr to expel carbon dioxide. 20 ml of $0 \cdot 02$N sodium hydroxide was then added. The suspension was shaken for 2 days, decanted (or centrifuged where necessary), and the supernatant liquid titrated with standard acid using bromothymol blue as the indicator. The solutions were boiled to expel carbon dioxide. This procedure was used for all the activated carbons but could not be used for the carbon blacks, because they dispersed to a colloidal suspension in alkali which could not be separated. This difficulty was overcome by using a $0 \cdot 02$N solution of alkali containing 10 per cent. sodium chloride. With " Black Pearl 2 ", 70 ml of $0 \cdot 02$N sodium hydroxide was used because of its abnormally high acidity.

Towards the end of the investigation it was found that the above procedure did not expel all the carbon dioxide and so gave high acidities. The following method was devised and used in the later experiments.

$1 \cdot 000$ g of carbon was added to a weighed tube, 10 ml of distilled water was added, and the suspension boiled under reflux for 1 hr to expel carbon dioxide. The tube was then stoppered and after cooling weighed to determine the amount of water present. The standard alkali solution was then added and the usual procedure followed.

(iv) *Sodium Methoxide Adsorption.*—$1 \cdot 000$ g of carbon was weighed into a 50 ml flask, a few ml of dry benzene was added, and the mixture boiled under reflux to expel carbon dioxide. The flask was then cooled, stoppered, and reweighed to give the weight of benzene added. A standard sodium methoxide solution was prepared by adding freshly cut sodium to 75 ml of dry methanol which was made to 1 l. with dry benzene. This was standardized potentiometrically against $0 \cdot 02$N benzoic acid. 20 ml of the standardized sodium methoxide and 15 ml of dry n-butylamine were added to the above carbon and the mixture shaken for 2 days. The suspension was then filtered under pressure to prevent loss by evaporation, and 15 ml aliquots of the filtrate collected. 15 ml of the $0 \cdot 02$N benzoic acid was added and the solution potentiometrically back-titrated with the standard sodium methoxide using a glass-antimony electrode system (Fritz and Lisicki 1951).

(v) *Hydrochloric Acid Adsorption.*—The adsorption of hydrochloric acid was determined by adding $1 \cdot 000$ g of carbon to 10 ml of water which was allowed to stand for 2 hr. 20 ml of $0 \cdot 02$N hydrochloric acid was then added and the

suspension shaken for 2 days.   The suspension was decanted (or centrifuged if necessary) and the supernatant liquid boiled and titrated with standard alkali using bromophenol blue as the indicator.

(vi) *Air Oxidation.*—" H " and " L " carbons were placed in an oven at 105 °C for 4 hr and also for 14 days with free access to air.   At the end of these periods their ability to adsorb acid and alkali was measured.

The same original samples were wetted with water.   Some were dried in air at 20 °C while the others were dried in the oven at 105 °C.   After drying, their ability to adsorb acid and alkali was again estimated.

(vii) *Suspension pH.*—1·000 g of carbon was suspended in 50 ml of distilled water and agitated with a stream of oxygen-free nitrogen.   The pH of the suspension was measured with a glass-electrode pH-meter until a steady state had been achieved.

(viii) *Ultimate Analysis.*—The carbon, oxygen, hydrogen, and ash content of the carbons were determined by the standard organic technique of combustion. Because many of the carbons were hygroscopic it was not possible to perform these measurements with oven-dried material.   Accordingly, the samples were air-conditioned overnight.   The analytical results thus include any adsorbed water present on the carbon.   A series of samples was heated in a vacuum at 80 °C, reweighed, and the analytical results recalculated on the assumption that the loss in weight was entirely due to the removal of moisture.

(ix) *Iron Estimation.*—A weighed sample of carbon was ashed.   The ash was dissolved in hydrochloric acid containing some nitric acid, evaporated to dryness to remove nitric acid, and then redissolved in hydrochloric acid.   The solution was made up to volume in a 25 ml flask.   5 ml aliquots were taken, a few drops of thioglycollic acid were added, and the solution made up to volume with 1 : 1 ammonium hydroxide.   The sample was compared in a Spekker absorptiometer with a standard prepared in the same way from ferrous ammonium sulphate.

(x) *Reduction of Silver Nitrate.*—The reducing property of the carbon was estimated by its ability to reduce silver nitrate.   1·000 g of carbon was shaken for 1 day with 25 ml of a 0·5N solution of silver nitrate containing 10 ml of conc. ammonia.   The carbon was filtered, washed with distilled water, and suspended in 20 ml of saturated potassium chloride for 10 min to precipitate any adsorbed silver ions.   The carbon was washed again with water, and then boiled for 1 hr in 7–8N nitric acid to dissolve any silver reduced by the carbon. The solution was separated from the carbon and its silver content estimated by titration with 0·1N potassium thiocyanate.

(xi) *Iodine Test.*—1·000 g of carbon was shaken for 1 hr with a 1N solution of iodine in dry benzene.   The carbon was then extracted with benzene for several weeks to free it from physically adsorbed iodine.   Extraction ceased 7 days from the time when a colour due to iodine could not be detected in the washings when a sample, 20 cm deep, was observed in a Nessler tube.   After drying, the iodine content of the carbon was estimated by the Parr bomb method.

(xii) *Magnetic Measurements.*—These were performed with a Gouy balance by Mr. Figgis of the N.S.W. University of Technology.   The carbons showed a

marked tendency to stratify during the normal packing procedure due to the separation of layers according to particle size. Accordingly Mr. Figgis adopted the following method of packing : the tube was filled with the loose material, then tapped to pack the material, and the excess removed. This procedure lowers the accuracy of the measurement of the absolute susceptibility, but allows more accurate comparison of the relative susceptibilities of the different carbons.
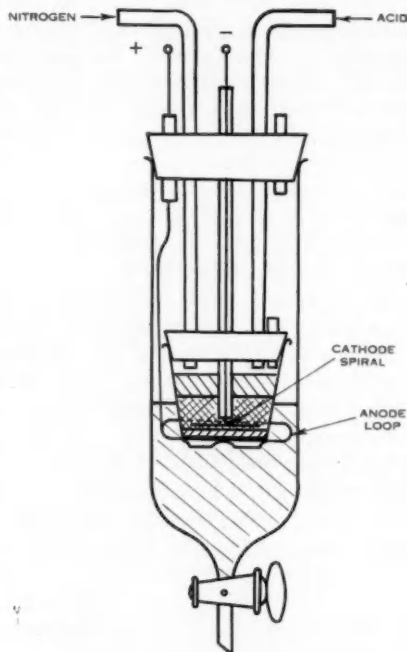
Fig. 1.—Cell for electrolytic reduction.

(xiii) *Electrolytic Reduction.*—" H " carbons were electrolytically reduced in the cell shown in Figure 1. A bed of the carbon to be reduced lay on a spiral of platinum wire placed on a sintered glass plate and formed the cathode. The anode consisted of a ring of platinum wire around the outside of the container holding the carbon. A solution could be percolated through the cathode material and continuously removed from the anode compartment. Provision was made for flushing the solutions and also the cathode compartment of the cell with nitrogen freed from oxygen.

In one experiment, a solution of oxygen-free 2N sulphuric acid was passed through the cell for 24 hr to remove peroxygen complexes* on the carbon followed

* King (1933) extracted peroxides from an " H " carbon with sulphuric acid. On re-exposure to air a further amount of peroxide could be extracted.

by a solution of $0 \cdot 0014$N sulphuric acid also freed of oxygen. After a further 24 hr a potential of 90 V was applied to the electrodes to pass a current of about 8 mA for 72 hr. The electrolysis proceeded with the cathode compartment flushed with nitrogen. During this period a dark layer appeared at the bottom of the anode compartment. This was found to be colloidal carbon. A blank experiment was performed under similar conditions except that a potential was not applied.

The experiment was repeated by electrolysing a fresh sample of carbon in a stationary layer of $0 \cdot 0014$N sulphuric acid. No precautions were taken to exclude oxygen from the cathode compartment. A corresponding blank was performed. This experiment was made with C_{800}^4 and the purified " H " carbon C_{800}^2. It was also repeated with C_{800}^4 using $0 \cdot 0014$N hydrochloric acid as the electrolyte.

After reduction all the carbons were washed with water for 3 days and their ability to adsorb acid and alkali then determined. Part of the reduced carbon C_{800}^4 was air dried while the remainder was dried in an oven at 105 °C for 4 hr before estimating the acid and alkali adsorption.

(xiv) *Potentiometric Titration.*—$1 \cdot 000$ g aliquots of carbon and 20 ml of distilled water were placed in weighing bottles, the volume marked and then boiled down to about 10 ml to expel carbon dioxide. The bottles were stoppered, cooled to room temperature, and then opened in an atmosphere of nitrogen. The volume was made up to 50 ml with boiled distilled water and various amounts of sodium hydroxide. The bottles were stoppered and shaken for 48 hr. The pH of the suspensions was then measured in an atmosphere of nitrogen until a steady reading was obtained. Aliquots of 1 m-equiv of acetic acid were used in place of the carbon and the procedure was repeated.

(xv) *Surface Areas.*—The surface areas of the activated carbons used were determined by the B.E.T. method in which nitrogen was used as the adsorbate. The carbon was outgassed at 100 °C until a vacuum of 10^{-4} mm could be maintained. The values of the surface areas of the carbon blacks are those given by the manufacturers in their trade literature.

(xvi) *Photographic Exposures.*—$0 \cdot 5$ g of various chars and carbon blacks were exposed in the dark for 5 days at 70 °C to Ilford Soft Gradation Panchromatic plates with an air space of 2 mm left between the samples and the photographic emulsion. The plates were then developed in the usual way.

(b) Results

The results of the various chemical tests on the activated sugar carbons, expressed on a weight basis, are summarized in Table 1. In Table 2 the same results are expressed on the basis of 100 m² of surface area. Table 3 presents similar data for the carbon blacks whereas Table 4 shows the same data expressed on the basis of 100 m². It can be seen from these results that the behaviour of the carbon blacks closely parallels that of the activated carbons and that whereas " Black Pearl 2 ", for example, conforms with Steenberg's definition of an " L " carbon, the properties of " Kosmos 20 " are those of an " H " carbon.

TABLE 1

EFFECT OF ACTIVATION TEMPERATURE ON THE PROPERTIES OF SUGAR CARBON

Results not corrected for surface area

Properties	Carbon Number										
	C^1_{400}	C^1_{550}	C^1_{650}	C^1_{800}	C^2_{400}	C^2_{550}	C^2_{650}	C^2_{800}	C^3_{400}	C^3_{800}	C^4_{800}
Activation temp. (°C) ..	400	550	650	800	400	550	650	800	400	800	800
Surface area (m²/g) ..	40	400	390	480	30	—	—	380	350	330	—
pH	4·5	6·8	6·7	9·0	4·4	4·9	6·9	7·1	5·7	9·0	7·2
Carbon (%)	75·7	85·2	87·3	94·3	80·8	87·3	94·0	95·7	79·2	93·5	96·3
Oxygen (%)	19·0	10·4	7·4	3·2	15·1	8·9	2·8	2·2	16·8	2·0	1·6
Hydrogen (%) ..	3·2	2·7	2·1	1·5	3·1	2·8	1·9	1·1	3·2	1·6	1·4
Ash (%)	0·7	1·33	1·44	1·23	0·036	0·068	0·082	0·265	0·46	0·70	—
Iron × 10³ (%) ..	1·5	0·42	1·6	1·4	0·13	0·49	0·21	0·17	0·37	1·7	—
Adsorption (μ-equiv/g)											
NaOH	340	159	158	23	392	343	217	114	312	12	30
HCl	39	155	169	265	19	106	220	249	55	300	204
NaOH boiled ..	—	—	—	—	191	159	5	0	—	—	26
MeONa	—	—	—	—	204	211	32	48	—	—	—
I₂	—	—	—	—	0	105	300	350	64	81	—
AgNO₃ reduced (m-equiv/g) ..	—	—	—	—	1·07	0·62	0·32	0·50	1·96	0·74	—
Magnetic measurements Temp. (°C)	24·3	24·3	24·3	24·6	24·3	24·3	24·3	24·3	—	—	—
χ × 10⁶/g ..	+3·27	+0·22	+2·04	+2·76	−0·32	−0·13	−0·09	−0·34	—	—	—
Approx. rel. error (%)	±3	±50	±4	±3	±25	±40	±40	±25	—	—	—

It should be noted that Steenberg's definition only refers to the behaviour of the carbon towards acids and alkalis. Two carbons having different types of acidic groups could conform to his definition of an " L " carbon but be quite different chemically. From the results on the carbon blacks selected for this

TABLE 2

EFFECT OF ACTIVATION TEMPERATURE ON THE PROPERTIES OF SUGAR CARBON

Results corrected for surface area

Properties	Carbon Number							
	C^1_{400}	C^1_{550}	C^1_{650}	C^1_{800}	C^2_{400}	C^2_{800}	C^3_{400}	C^3_{800}
Activation temp. (°C) ..	400	550	650	800	400	800	400	800
Adsorption (μ-equiv/100 m²)								
NaOH	850	40	40	4·8	1310	30	89	3·6
HCl	98	39	41	56	63	66	16	91
NaOH boiled	—	—	—	—	630	0	—	—
MeONa	—	—	—	—	680	13	—	—
I₂	—	—	—	—	0	92	18	25
AgNO₃ reduced (m-equiv/100 m²) ..	—	—	—	—	3·56	0·13	0·56	0·22

study, and also from Wiegand's (loc. cit.) experiments,* it appears that the pigment blacks and very acid channel blacks are " L " carbons, high abrasion furnace blacks are " H " carbons, and the others have characteristics which are intermediate between the extreme " H " and " L " forms. This form of classification will be tentatively adopted in the subsequent discussion.

TABLE 3

PROPERTIES OF SOME TYPICAL CARBON BLACKS

Results not corrected for surface area

Properties	Carbon Blacks			
	" Black Pearl 2 "	" Kosmos H.M."	" Spheron 3 "	" Kosmos 20 "
pH	3·9	4·5	5·0	7·5
Surface area (m²/g)	850	120	142	20
Carbon (%)	80·5	93·3	94·2	98·2
Oxygen (%)	13·2	5·8	4·6	0·7
Hydrogen (%)	1·9	1·1	1·2	0·7
Ash (%)	0	0	0	0·91
Adsorption (μ-equiv/g)				
NaOH	1150	172	142	0
HCl	46	37	44	45
I₂	48	57	81	30
AgNO₃ reduced (m-equiv/g)	1·04	0·53	0·54	0

TABLE 4

PROPERTIES OF SOME TYPICAL CARBON BLACKS

Results corrected for surface area

Properties	Carbon Blacks			
	" Black Pearl 2 "	" Kosmos H.M."	" Spheron 3 "	" Kosmos 20 "
pH	3·9	4·5	5·0	7·5
Adsorption (μ-equiv/100m²)				
NaOH	135	144	100	0
HCl	5·4	31	31	225
I₂	5·6	47·5	57	150
AgNO₃ reduced (m-equiv/100 m²)	0·12	0·44	0·38	0

It is seen from Tables 1–4 that the presence of carbon dioxide results in high acid values as determined by the usual sodium hydroxide procedure. The

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* Wiegand showed that the various carbon blacks could be classified into distinct groups according to the pH of their aqueous suspension. His so-called " chemisorption " measurements with diphenylguanidine are probably akin to our measurements with sodium hydroxide.

results for the boiled carbons agree fairly well with those determined by the sodium methoxide method and the trend is the same as with the unboiled samples.

It is also seen that the presence of iron in the carbon does not affect the relative qualitative behaviour of the carbons activated at various temperatures, but when its concentration is reduced the iodine adsorption is considerably

TABLE 5

EFFECT OF MOISTURE ON THE ULTIMATE ANALYSIS OF SUGAR CARBONS

Moisture	Carbon Number			
	C_{400}^2	C_{550}^2	C_{650}^2	C_{800}^2
Loss in weight (%)				
(80 °C/0·1 mm vac.) ..	3·40	1·69	1·00	0·86
Based on original				
Oxygen (%)	15·1	8·9	2·8	2·2
Carbon (%)	80·8	87·3	94·0	95·7
Hydrogen (%)	3·1	2·8	1·9	1·1
Ash (%)	0·20	0·13	0·22	0·15
Based on dried carbon				
Oxygen (%)	12·5	7·5	2·1	1·5
Carbon (%)	83·7	88·8	94·9	96·7
Hydrogen (%)	2·8	2·6	1·8	1·1
Ash (%)	0·21	0·13	0·22	0·15

TABLE 6

AIR OXIDATION OF SUGAR CARBONS

Treatment	" L " Carbon		" H " Carbon	
	HCl ads. (μ-equiv/g)	NaOH ads. (μ-equiv/g)	HCl ads. (μ-equiv/g)	NaOH ads. (μ-equiv/g)
Original sample	18	108	204	30
4 Hours at 105 °C ..	12	96	150	30
14 Days at 105 °C	6	190	60	30
Wetted and dried at 20 °C	18	104	89	32
Wetted and dried at 105 °C				
for 4 hr	24	132	48	36

increased. Some important trends are apparent. Thus acid and iodine adsorption and also the pH value of the water suspension increase with activation temperature whereas alkali adsorption and the ability to reduce silver nitrate decrease. An exception is the acid uptake of C_{400}^1 when expressed on the basis of 100 m² of surface area. Its acid adsorption exceeds that of the other carbons

in the series, but the ratio of alkali to acid adsorption decreases as the temperature of activation increases.

The loss of weight, which occurs when various sugar carbons are heated to 80 °C in a vacuum of 0·1 mm to constant weight, is recorded in Table 5. The assumption was made that this loss was due to the liberation of water vapour and the results of the ultimate analysis of the air-conditioned carbons were recalculated on this basis. This assumption is not strictly correct since volatile matter other than water is undoubtedly liberated as well. Since this method

TABLE 7

ELECTROLYTIC REDUCTION OF " H " CARBONS

Method of Reduction	O (%)	H (%)	NaOH ads. (μ-equiv/g)	HCl ads. (μ-equiv/g)
Original carbon C_{800}^4				
R3 Electrolytic, H_2SO_4 and absence O_2, oven dried	3·5	1·6	162	48
,, blank, oven dried	3·0	1·4	36	30
R4 Electrolytic, H_2SO_4 and presence O_2, oven dried	3·3	1·5	126	60
,, blank, oven dried	3·7	1·7	30	30
Original carbon C_{800}^4				
R5 Electrolytic, HCl and presence O_2, oven dried, not boiled.. ..	3·1	1·5	96	42
,, HCl and presence O_2, oven dried, boiled*	—	—	122	35
,, HCl and presence O_2, air dried, not boiled.. ..	—	—	122	70
,, HCl and presence O_2, air dried, boiled*	—	—	106	64
,, blank, oven dried, not boiled	6·6	1·9	42	48
Original carbon C_{800}^2				
R6 Electrolytic, H_2SO_4 and presence O_2, oven dried	6·5	1·9	168	108
,, blank, oven dried	4·9	1·5	30	96
,, ,, air dried	—	—	39	136

* The carbon was boiled before estimating its NaOH adsorption (see Section V (a) (iii)).

does not give absolute results the simpler procedure of air-conditioning was adopted throughout the work. The oxygen and hydrogen contents of the carbons decrease with increase in activation temperature and this trend is apparent with both methods of analysis. The hygroscopic character is more pronounced with an " L " than with an " H " carbon.

Table 6 shows the behaviour of an " H " and " L " carbon towards oxidation. The inability of an " H " carbon to adsorb alkali is not impaired by drying in air or heating to 105 °C for long periods, but heating reduces the ability of an

" H " carbon to adsorb acid and the effect is enhanced by moisture. The adsorption of acid by an " L " carbon is not greatly affected by heating or

TABLE 8

PROPERTIES OF A CHLORINATED " L " CARBON

" L " Carbon			Chlorine (%)	Adsorption (μ-equiv/g)	
				NaOH	HCl
Original C_{400}^3	..	..	0	312	55
Chlorinated	..	..	35	36	12

moisture, but the adsorption of alkali increases on heating, and the effect is accentuated by moisture. These results indicate the need for caution in interpreting the results of the adsorption of acid by carbon.
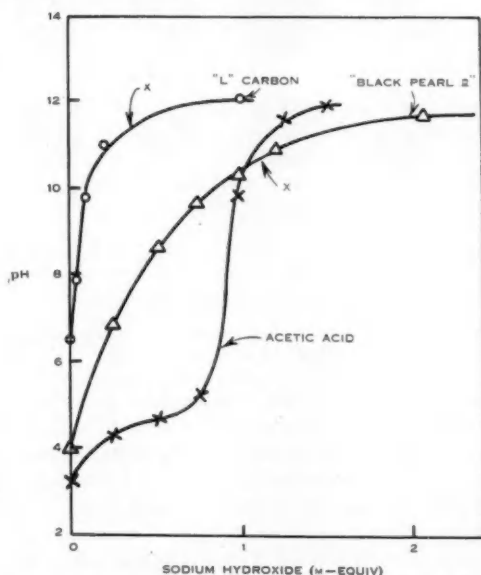
Fig. 2.—Potentiometric titration curves of sugar carbon C_{400}^3 and " Black Pearl 2 ".

When an " H " carbon is reduced electrochemically a marked increase occurs in its ability to adsorb alkali (Table 7). The presence of gaseous oxygen in the electrolyte cell during electrolysis does not significantly affect the results. Nor is the nature of the acid used as an electrolyte of any importance. Since

the reduced carbons and those used in the control experiments had to be dried no significance can be attached to the acid adsorption values.

When the " L " carbon C_{400}^3 was chlorinated it chemisorbed 35 per cent. by weight of chlorine and lost almost completely its ability to adsorb acid and alkali (Table 8).

The titration curve for the " L " carbon C_{400}^3, " Black Pearl 2 " and an equivalent amount of acetic acid is given in Figure 2. The crosses (Fig. 2) show the position on the curves corresponding to the alkali adsorption presented in Tables 1 and 3. This clearly shows that the alkali test is purely empirical and does not quantitatively measure the total concentrations of acidic groups on the carbon.
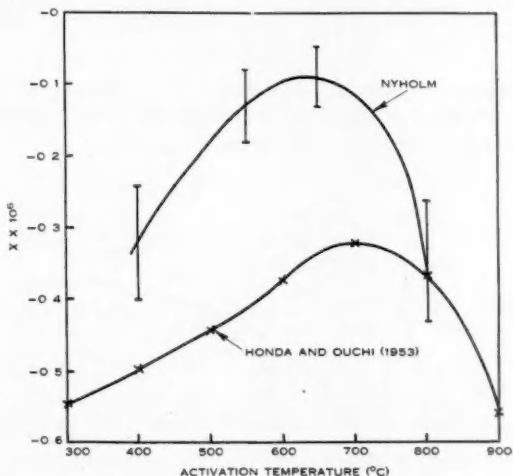
Fig. 3.—Effect of activation temperature on the magnetic susceptibilities of sugar carbons.

" L " carbon C_{400}^3 was extracted with acetone in a Soxhlet extractor for 24 hr and then washed with a continuous stream of cold distilled water for 2 days. The acid and alkali adsorption of the washed carbon was not significantly altered by the extraction thus establishing that the adsorption of these substances was either a property of the carbon surface itself or of adsorbed substances insoluble in acetone.

" L " type carbons strongly fog a photographic plate but " H " carbons do so to a considerably lesser extent (Plate 1).

Figure 3 shows that the diamagnetic susceptibility of the low ash carbons plotted as a function of the temperature of activation is a minimum in the region of 650 °C. The results of Honda and Ouchi (loc. cit.) with chars prepared from glucose are also plotted on the same graph and are qualitatively similar. The carbons C_{400}^1, C_{550}^1, C_{650}^1, and C_{800}^1, which contain considerable amounts of iron, show a minimum in paramagnetic susceptibility when activated in the

QUINONE-HYDROQUINONE CHARACTER OF CARBON
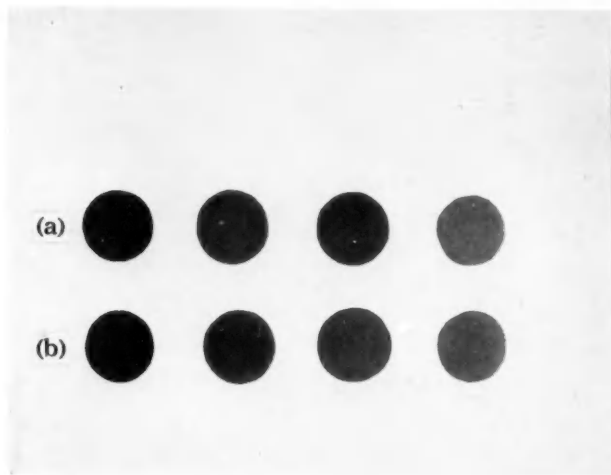
Effect of exposing a photographic plate to various sugar carbons and carbon blacks in the dark.

(a) Left to right: Sugar carbons C_{400}^2, C_{550}^2, C_{650}^2, and C_{800}^2.

(b) Left to right: Carbon blacks "Black Pearl 2", "Kosmos H.M.", "Spheron 3", and "Kosmos 20".

region of 650 °C (Table 1). These values can only be accounted for if the iron is present in a ferromagnetic state. The magnetic measurements must be interpreted cautiously since the carbons contain various amounts of iron. It is therefore not possible to estimate the single-electron concentration of the various carbons from these measurements.

VI. DISCUSSION
(a) The Quinone Character of " H " Carbons

When an " H " carbon is reduced it becomes markedly acidic and is in accordance with Steenberg's definition of an " L " carbon. The cause of this acidity may be deduced from the following arguments. An analysis established that sulphur is absent in the " H " carbon so sulphydryl groups could not have been produced on reduction. Carbonyl oxygen present as a ketone or aldehyde group would yield an alcohol on reduction, and ether oxygen would not be reduced at all. Molecular oxygen or peroxygen cannot play any part in the development of acidity during reduction since the same results were obtained in their presence as in their absence. The acidity may therefore be attributed to the presence of phenolic groups of a hydroquinone character and it can be concluded that quinonoid groups must be present in an " H " carbon. This is in accordance with the findings of Kmetko (1951) who measured the infra-red absorption spectrum of films of " Cellophane " that had been charred at various temperatures. A slight absorption peak was present at a wavelength in the region of 6 μ in the film charred at 350 °C and was intensified in the film charred at 500 °C. The film was not transparent above 630 °C. Flett (1948) has shown that the quinone oxygen group has a characteristic absorption at 5·96 μ. From a study of the combustion of graphite, Sihvonen (1938) concluded that carbonyl or ketene groups at the solid surface or crystal edge are formed as intermediates. Electrolytic experiments with graphite cathodes led him to suggest that keto groups were present which could be reduced to alcohols.

(b) The Hydroquinone Character of " L " Carbon

Steenberg has conclusively established that acidic groups are present on the surface of an " L " carbon which " adsorbs " sodium hydroxide by a process of neutralization. The following facts show that these are probably phenolic groups. The usual pK_a value of a carboxylic group is in the region of 4–5. A comparison between the titration curves of the " L " carbons and acetic acid (Fig. 2) shows that acidic groups of such a strength are absent. This suggests that carboxylic groups are absent* and that phenolic groups are responsible for the acidity of " L " carbons. It is possible that some enolic groups are also present in aliphatic side-chains attached to the aromatic nucleus. Villars (1947) also concluded that the acidity of an " L " type carbon was of a phenolic character.

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* It is highly probable that carboxylic groups are present on " L " carbons which have been allowed to undergo extensive autoxidation. They are substantially absent from freshly prepared " L " carbons probably because they are thermally unstable at 400 °C.

Our results suggest that some of these phenolic groups have hydroquinone characteristics since " L " carbons can reduce alkaline silver nitrate.   Kendall (1935) has shown that only polyphenols containing the $\underset{/}{HO}\diagdown\underset{/}{(C=C)_n}\diagup\overset{OH}{\diagup}$ structure are reducing agents.   If an " L " carbon is exposed to chlorine at 300 °C it chemisorbs chlorine and loses its ability to adsorb alkali.   This behaviour resembles that of p-benzohydroquinone which produces chloranil when treated with chlorine under oxidizing conditions (Datta 1914).
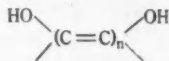
It may be concluded that the reduced " H " carbons are chemically similar to " L " carbons, and that " L " carbons have phenolic groups some of which at least have reducing properties and are separated from each other by an even number of carbon atoms in a conjugated system.   In accordance with this " H " carbons reduce silver nitrate to a smaller extent than " L " carbons. By analogy with benzohydroquinone, chlorination of an " L " carbon probably produces a chloranil type structure which does not adsorb alkali.

(c) Oxygen Structures in Carbons

If an " H " carbon is an oxidized form of an " L " carbon there should be a corresponding change in the ratio of oxygen to hydrogen in the two species. However, the analytical data presented cannot be used to determine this change since it seems certain that quinonoid oxygen only accounts for a small proportion of the total oxygen present in a carbon.   Thus Villars (loc. cit.) has provided evidence which suggests that the major oxygen content of channel blacks is ether oxygen.   Riley (loc. cit.) has shown that the size of the individual crystallites increases considerably as the activation temperature is increased from 400 to 800 °C.   Our results show that " H " carbons contain considerably less oxygen than do " L " carbons.   It is therefore possible that much of this ether oxygen occurs between the edges of the layer planes and is eliminated on heating. Since the primary reaction in the initial charring of sucrose or other carbohydrates is most likely one of condensation it is easily seen how ether oxygen could be incorporated into a carbon structure.   It is possible that some of this ether oxygen could be part of a ring structure analogous to that in the anthocyanins. If this were so the carbon should form an oxonium salt with dilute hydrochloric acid.   However, Steenberg showed that the adsorption of mineral acids from dilute solutions by activated carbon can be inhibited by the adsorption of non-electrolytes which suggests that the adsorption is due to short-range adsorption forces and not to salt formation.   It can therefore be concluded that such oxonium structures within the crystallites probably do not occur.

(d) The Electrokinetic Behaviour of " H " and " L " Carbons

The electrokinetic behaviour of unplatinized and platinized carbons is in accordance with their quinone or hydroquinone structures.   Bach (1941) extensively studied the electrokinetic properties of ash-free and platinized " H " and " L " carbons.   An ash-free carbon activated in hydrogen at 900 °C and cooled in hydrogen was electrokinetically positive.   The hydrogen was

thought to reduce surface oxides. However, work in this Laboratory has shown that the surface oxides of an " H " carbon are not reduced to phenols with hydrogen at 900 °C, since the carbon retains some of its original ability to adsorb acid and does not appreciably adsorb alkali. The oxygen content of the carbon does decrease and it is probable that this occurs by an initial reduction of the quinone groups followed by the loss of water since phenolic structures appear to be unstable at this temperature. We were not able to reduce an " H " carbon to an " L " carbon with hydrogen at 400–600 °C. The hydrogen in Bach's experiments therefore provides an atmosphere which prevents " L " carbon formation during the cooling period. When hydrogen-treated " H " carbon was heated in air at 450 °C for various times from 1·5 to 10 hr, Bach found that the carbon steadily lost its positive electrokinetic charge and became negative as the heating period increased. The pH of the suspensions steadily decreased on prolonged heating in air at 450 °C. These results can be simply explained since an " H " carbon probably acquires a positive charge because of its ability to preferentially adsorb hydrogen ions, and heating an " H " carbon in air at 400 °C produces surface acids which would give a negative electrokinetic charge.

Platinized carbons behaved differently. A carbon, impregnated with platinic chloride, which was heated at 980 °C in hydrogen and cooled in hydrogen, was electrokinetically negative when the suspension was in contact with hydrogen. The negative potential increased with increase in pH. When the same carbon was exposed to oxygen it became electrokinetically positive to an extent which increased with decrease in pH. The potential was zero at pH 8. These results of Bach are an extension of the earlier studies of platinized carbons by Frumkin (1930) who showed that a platinized carbon adsorbs acid but not alkali in the presence of oxygen at room temperature, but adsorbs alkali but not acid in the presence of hydrogen. When platinized carbon in an atmosphere of hydrogen is placed in a solution of sodium chloride the suspension becomes acidic, while in the presence of oxygen it becomes alkaline (Levina, Frumkin, and Lunev 1935). Bruns et al. (1932) obtained similar results by impregnating carbon with metals such as osmium, palladium, gold, and silver. The behaviour of the platinized carbons can also be accounted for if it is assumed that the presence of the platinum enables the carbons to be oxidized or reduced with oxygen or hydrogen at room temperatures. Thus a platinized " H " carbon can be reduced with hydrogen to an " L " carbon and the latter can be reoxidized with oxygen to an " H " carbon at room temperature.

(e) The Semiquinone Character of Carbon

Sugar carbons activated at temperatures between 500 and 700 °C can adsorb both acid and alkali, and some carbon blacks are similar. Hence such carbons will contain both quinone and hydroquinone groups. An aromatic structure containing quinone and hydroquinone groups linked by a common conjugated system of double bonds will partly acquire the properties of a semi-quinone in which resonance is set up between the various groups (Fig. 4). The semiquinone should not be regarded as an entity as such but as a resonance

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hybrid.* This type of resonance might reasonably be expected to extend over the whole conducting structure of the carbon.

When a carbon has excess hydroquinone groups, as compared with quinone groups, it acquires the properties of both a semiquinone and a hydroquinone (" L " carbon). When it has excess quinone groups it has the properties of both
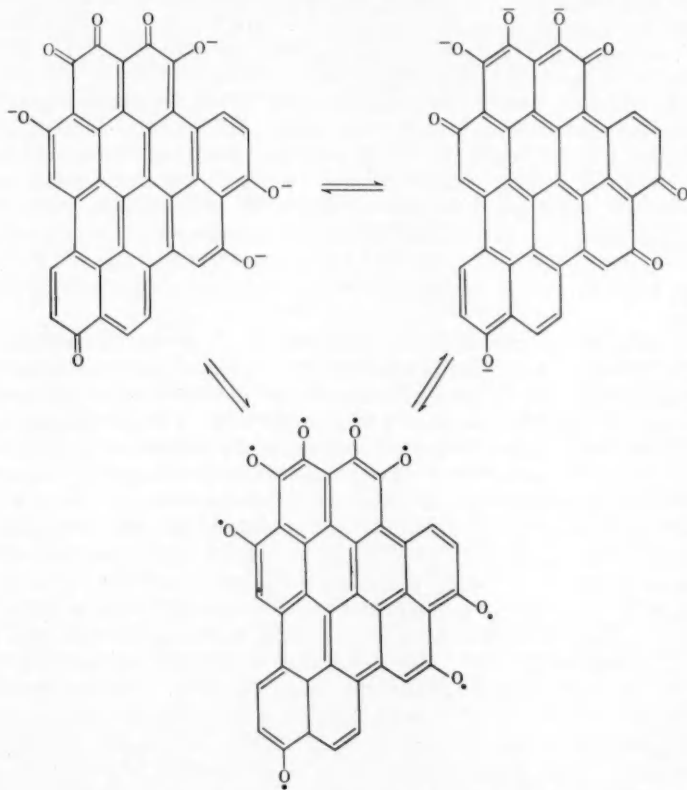
Fig. 4.—Resonance structures illustrating semiquinone formation.

a semiquinone and a quinone (" H " carbon). An " H " carbon without hydroquinone groups would not have any semiquinone character.

Such a semiquinone structure with its unpaired electrons† explains the ability of some sugar carbons to catalyse the ortho-para-hydrogen conversion

* Geake and Appleton (1941) showed that when an anthraquinone dye-stuff containing four quinone groups is reduced half-way a complex semiquinone results, which is strongly stabilized by the large number of different resonating structures that are possible.

† Michaelis and co-workers (1938) observed that semiquinones are paramagnetic.

(Bonhoeffer, Farkas, and Rummel 1933). However, Wynne-Jones and Blayden (1952) observed that various carbons were diamagnetic, and that carbon blacks were the least diamagnetic. Hence the diamagnetic graphitic structure of the carbon overshadows the paramagnetic contributions of the semiquinone groups.

The minimum in diamagnetic susceptibility of a char activated at about 600–700 °C observed by Honda and Ouchi (loc. cit.) and confirmed by our measurements (Fig. 3) occurs in the region where both acid and alkali uptake is observed. Recently Ingram *et al.* (1954) showed that the intensity of paramagnetic absorption by a series of carbons heated over the temperature range 20–800 °C was a maximum in the region of 550 °C. They suggested that this type of absorption is due to unpaired electrons possibly associated with free radicals. It can be explained by the presence of a maximum concentration of coexisting resonating hydroquinone and quinone structures. These results thus strongly support the concept of semiquinone structures in these carbons. The minimum in paramagnetic susceptibility observed with carbons that contain considerable amounts of iron may result from an interaction between the unpaired electrons of the ferromagnetic iron and the semiquinone structures. The stability, which Riley (1939) found, of a carbon towards oxidation with chromic acid was a maximum in this region. The semiquinone system of the carbon with its large number of resonating structures might account for this stability.
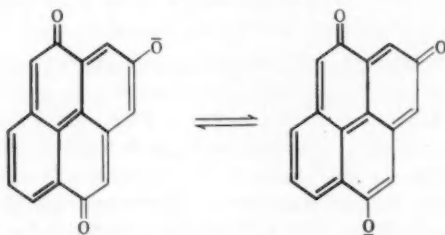
Fig. 5.—Fixation of double bonds by a non-resonating quinone group.

(f) The Olefinic Character of Carbon

The quinone structure of an " H " carbon results in the fixation of some of the double bonds of the carbon which lose their aromatic character and acquire that of an olefine.* The example in Figure 5 serves to illustrate this principle in a simple system. Thus the double bonds shown in heavy type are fixed and cannot resonate and are therefore olefinic, whereas the remainder are aromatic. It should also be noted that one quinone group can create a considerable number of olefinic double bonds. In contrast, a pure " L " carbon is essentially aromatic. Stearns and Johnson (1951) found that a channel black having the properties

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* The olefinic character of quinones is summarized by Fieser and Fieser (1944). *p*-Benzoquinone being an αβ-unsaturated carbonyl compound also acts readily as a partner in diene synthesis (Diels and Alder 1929). Maleic anhydride behaves analogously.

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of an " L " type carbon chemisorbed bromine and that the heat of this reaction was similar to that liberated during the bromination of low molecular weight olefines.   On heating to the corresponding " H " carbon the chemisorption increased and 4×10^{-4} mol/g of bromine were added whereas the original black only chemisorbed 1×10^{-4} mol/g.   The unsaturation of the channel black " L " carbon could arise from some quinone groups present on sites where they cannot participate in resonance.   Unsaturation in both " H " and " L " carbons could also be partially due to the presence of unsaturated side-chains attached to the aromatic nucleus.

Our results show that the irreversible adsorption of iodine by the " L " carbon C_{400}^{2} is zero but is considerable for the " H " carbon C_{800}^{2}.   With carbon blacks an upward trend in iodine adsorption is also observed with increase in " H " characteristics.   Since the magnetic susceptibilities of the carbons activated at 400 and 800 °C are of a similar order there appears to be no correlation between the iodine adsorption and the paramagnetic properties.   On the other hand an excellent correlation exists between the iodine adsorption and the quinonoid characteristics.   Stearns and Johnson found that graphitized carbon blacks did not react with bromine so that it is unlikely that the iodine adsorption can be due to the formation of interlamellar graphite compounds. It therefore appears that the mechanism of the iodine adsorption requires more detailed study before any definite conclusions can be drawn but it could be due to an addition to activated olefinic double bonds.

The presence of activated double bonds could explain the ability of carbon black to combine with, and cross-link, rubber polymers.   It can also be expected that furnace blacks are intrinsically more strongly reinforcing than channel blacks of the same particle size because of their more pronounced quinonoid character.   Graphitic carbon blacks of the " Graphon " type lack reinforcing properties (Stearns and Johnson loc. cit.).   This is undoubtedly because quinone oxygen has been removed at 1200–1400 °C in the course of the high temperature processing used in graphitizing these carbons.   This subject is reviewed by Scott (1951).   The significance of this fact in rubber reinforcement and the reactivity of carbon blacks towards various free radicals is discussed by Garten and Sutherland (1954).

(g) Chemisorption

Three different types of chemisorption may occur on " L " and " H " carbons.

(i) Substitution reactions may occur. Thus considerable amounts of hydrochloric acid are produced when an " L " carbon is heated in a stream of chlorine and the resulting carbon contains chemisorbed chlorine.

(ii) Addition reactions may take place in which two atoms are added to one double bond.   The chemisorption of bromine is one example.

(iii) Addition of a single free radical to one double bond may also occur as a consequence of the quinone structure of the carbons since quinones react

readily with single free radicals forming a substituted quinone and a semi-quinone. The latter can disproportionate to a quinone and a hydroquinone. For example, a styrene free radical adds on to benzoquinone, and hydroquinone can be recovered from the reaction mixture (Fieser and Oxford 1942).
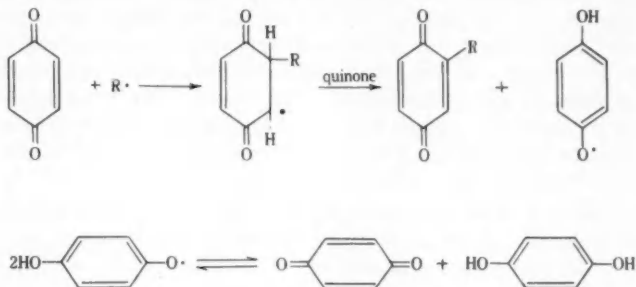
Similarly Garten and Sutherland (loc. cit.) found that styrene free radicals are chemisorbed by various carbon blacks. Likewise when benzidine was half-oxidized to an intermediate free radical stage it was readily chemisorbed by " L " and " H " carbons. The chemisorption was greater with " H " than with " L " carbons.

(h) The Adsorption of Acids by " H " Carbons

The olefinic bonds of an " H " carbon resulting from its quinonoid structure will add on molecular oxygen to form peroxygen groups.* This accounts for their known presence on activated carbon (Winslow 1947). Oxygen added to a double bond adjacent to a quinone group can be expected to cause an electromeric shift of electrons which increases the dipole charge on the structure.† The small adsorption of acid by an " H " carbon may be the result of a weak electrostatic interaction between these dipole charges and the acid and this adsorption would be inhibited by high concentrations of polar non-electrolytes as observed by Steenberg (1944). When a carbon is out-gassed in a vacuum at 950 °C the peroxygen is removed. Burstein and Frumkin (1929) showed that a thoroughly out-gassed " H " carbon completely lost its ability to adsorb acid but regained it on exposure to air at room temperature. These results suggest

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* It has been established that in conjugated olefinic systems the addition of oxygen to the double bonds gives rise to 1–2 or 1–4 addition with the formation of peroxides rather than hydroperoxides (Schenck 1949). Ketones having conjugated double bonds adsorb oxygen whereas those without them do not (Treibs 1930). Benzoquinone in solution reacts with molecular oxygen, particularly under alkaline conditions, and darkens (Florence and Bessieres 1943a, 1943b).

† Nagakura and Kuboyama (1954) have studied the dipole moments and distribution of π-electrons in simple quinones. These were found to have abnormally high dipole moments. The π-electron migration from carbon atoms in the ring to oxygen atoms increases with the addition of further benzene rings.

that the quinone groups cannot of themselves induce a sufficient dipole charge for appreciable acid adsorption to occur in dilute solutions of acids. However, by analogy with the behaviour of simple quinones, it is most likely that oxonium salts could be formed in concentrated solutions of acids.

Bruns and Puizhov (1931) found that the adsorption of acid by an " H " carbon from an aqueous solution is increased in the presence of ozone and the increase is greater than that occasioned by oxygen. Carbon that has been subjected to the action of ozone under these conditions does not adsorb sodium ions from aqueous sodium hydroxide. This result could be explained by the formation of an ozonide instead of a peroxide and the oxidation of any hydroquinone groups to quinones. The ozonide would have a greater inductive effect and might therefore adsorb acid more strongly.

It can be concluded that the ability of a carbon to adsorb mineral acid is probably indicative of the presence of a quinone structure and its resulting peroxygen. In accordance with this an " L " carbon, which adsorbs less acid than an " H " carbon, has a less developed quinone character and less pronounced olefinic properties.

(i) Air Oxidation

" L " carbons contain a few quinone groups and an appreciable concentration of phenolic groups of the hydroquinone type. The olefinic bonds of the quinonoid system might add on oxygen as shown in Figure 6 to form a peroxygen compound, one possible structure of which is I. This could then oxidize an ionized hydroquinone group by abstracting an electron and rearrange to form structure II containing a monovalent peroxygen anion. This reaction is analogous to the addition of single free radicals to simple quinones, where the excess electron is stabilized by reducing a second quinone group to the resonance stabilized semiquinone. Compound II then abstracts a second electron from another hydroquinone group or a semiquinone and liberates a divalent oxygen anion which, with a hydrogen ion from the water, can form a peroxide anion (IIIa).

It could also react according to IIIb in which the peroxygen anion splits and reacts with water to form a molecule of hydrogen peroxide and an ionized hydroxyl group permanently attached at the original point of attack.

A pure " H " carbon could not liberate hydrogen peroxide in this manner, since it does not possess any electron donors. If electrons are supplied by an external source it might be expected to become an effective catalyst for the ionization of oxygen because it forms peroxidic complexes most readily. Berl (1943) showed that activated carbon functions as an oxygen electrode which reversibly reduces oxygen to hydrogen peroxide. Unfortunately he did not indicate the manner in which the carbon was prepared. According to the above concept " H " carbons should function more effectively than " L " carbons as oxygen electrodes but further experimental data are required. Similarly many vat dyes in the presence of electron donors produce hydrogen peroxide when oxidized (Atherton and Turner 1946). Manchot (1901a, 1901b) observed that hydrogen peroxide is formed when anthrahydroquinone absorbs oxygen.
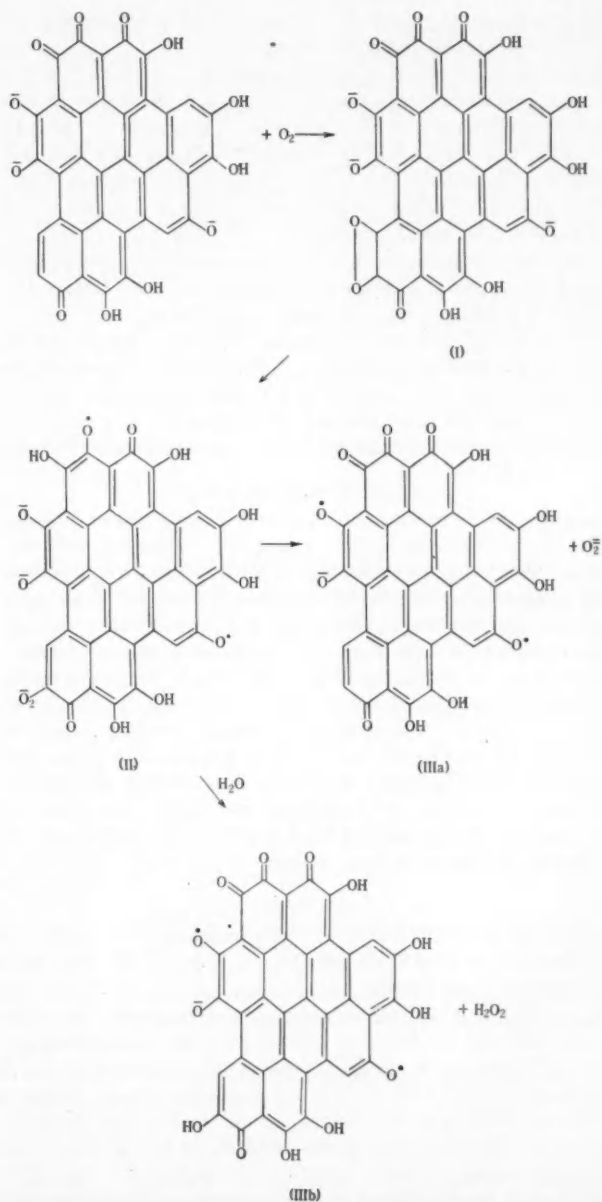
Fig. 6.—Hydrogen peroxide production by a polynuclear aromatic structure containing quinone and hydroquinone groups.

This has led to a technical process for the production of hydrogen peroxide using 2-ethylanthrahydroquinone (I.G. Farbenindustrie 1937).

The reversibility of these processes suggests that both " H " and " L " carbons can catalyse the ionization of oxygen by a mechanism analogous to that of IIIa provided an external source of electrons is available for the " H " carbon.

On the other hand there is also evidence which suggests that the oxidation may proceed by mechanism IIIb. Thus King (1934) showed that an " H " carbon which initially catalysed the decomposition of hydrogen peroxide lost its activity rapidly and became acidic.*

From the available evidence it is thus not possible to decide whether there is joint or exclusive operation of the mechanisms IIIa and IIIb.

The observed fogging of a photographic plate by an " L " carbon (Plate 1) could be due to liberated hydrogen peroxide since it is well known that the latter readily fogs a photographic plate. This is the accepted explanation of the Russell effect. An " H " carbon which does not adsorb any alkali is not able to spontaneously liberate hydrogen peroxide and fog a photographic plate since hydroquinone groups are not present to act as electron donors.

(j) Free Radical Structures

A further possibility exists that quinonoid groups placed in some positions on the edges of the crystallites could result in structures containing trivalent carbon atoms. This is illustrated in Figure 7 by a simple hypothetical structure which might be capable of existing in a number of resonant forms some of which are shown. The asterisk marks the presence of the trivalent carbon. Similar types of structures could arise from imperfections in the crystallite structures due to the presence of five-membered rings. Such structures could account for the irreversible adsorption of iodine, and the reactivity of the carbon towards free radicals and oxygen. The presence of such structures could not account for the minimum in diamagnetic susceptibility which has been observed. It must therefore be concluded that if they do exist at all they must be accompanied by the quinone-hydroquinone structures previously described. Since the purified " L " carbon C_{400}^2 did not irreversibly adsorb any iodine such free radicals cannot be present in this particular carbon.

(k) Fuels

Although a detailed discussion of the significance of the quinone-hydroquinone structures to carbon fuel chemistry is beyond the scope of this paper some general remarks are pertinent.

Sodium carbonate is known to enhance the reactivity of cokes towards steam and this may well be due to an ionized phenolic group which can be more readily oxidized than an un-ionized group. Thus hydroquinone is readily oxidized by air in alkaline solution but not in acid solutions. Since resonating semiquinone structures can only occur by an interaction between quinone groups and ionized phenolic groups the addition of alkali to a carbon should

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* p-Benzoquinone is readily attacked by dilute hydrogen peroxide to form hydroxyhydroquinone (Mees 1948).

increase the concentration of single unpaired electrons. Our magnetic results suggest that such structures readily interact with paramagnetic ash constituents and hence as a result it is most likely that the catalytic activity of the ash and hence the reactivity of the carbon will be affected.

It is well known that the oxygen content of a carbon is eliminated over the temperature range of 1200–1400 °C and this suggests the loss of quinone structures at these temperatures. It is possibly more than coincidental that it is in this region that Honda and Ouchi (loc. cit.) observed that the rate of change of
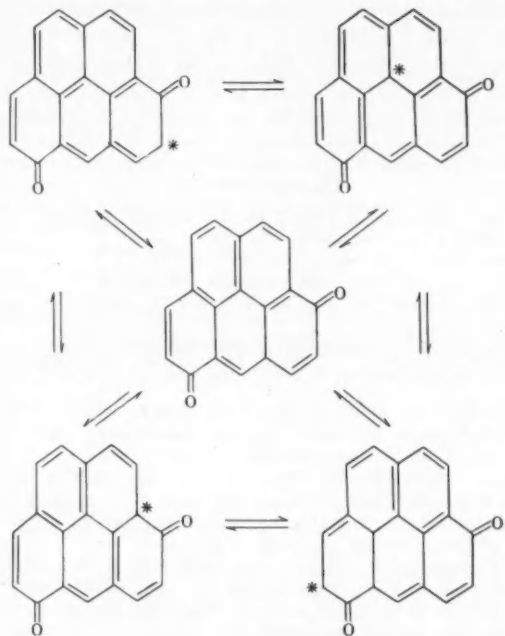
Fig. 7.—Hypothetical aromatic structures showing resonating trivalent carbon.

diamagnetism with temperature increases sharply and that Strickland-Constable (1944) showed that the oxidation of carbon changes from a first order reaction to one of zero order.

However, before any definite conclusions can be drawn concerning these proposals more experimental data are required.

VII. CONCLUSIONS

The following conclusions can be made from the above arguments. " L " carbons are essentially aromatic structures containing phenolic groups, some of which possess reducing properties. " H " carbons contain quinone groups

which impart some olefinic characteristics to the carbon. This accounts for the ability of the latter to " reinforce " rubber, to function as an oxidizing agent, to form peroxides, and to catalyse the ionization of oxygen in the presence of an electron donor. The more usual structure is intermediate between the " L " and " H " extremes and, owing to electronic interaction between these coexisting structures, contains a significant number of semiquinone groups.

VIII. Acknowledgments

The authors are grateful to all who have contributed to this paper, and particularly to Messrs. R. McNeill, M. Ross, and H. P. Rothbaum who performed the experimental work ; to Professor R. Nyholm (N.S.W. University of Technology) for supplying the magnetic data, to Dr. W. Zimmerman for performing the ultimate analyses, and also to Dr. H. H. Hatt, Dr. K. L. Sutherland, Dr. J. D. Blackwood, Mr. G. Ingles, and Dr. A. L. G. Rees of this Division for helpful discussions.

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REDUCTION BY DISSOLVING METALS

XII. THE CONVERSION OF 2,5– INTO 2,3–DIHYDROANISOLES BY MEANS OF POTASSIUM AMIDE IN AMMONIA

By A. J. Birch* and Patricia Hextall*

Summary

The direction of the conjugation of double bonds in some 2,5-dihydroanisole derivatives has been further examined.

I. Introduction

Reduction of many anisole derivatives by alkali metal-alcohol-liquid ammonia reagents leads to the corresponding 2,5-dihydroanisole (e.g. I) (Birch 1944). Further reduction of these can occur through the conjugated 2,3-dihydroanisole (e.g. II) derivatives obtained by the action of metal amides in liquid ammonia. A knowledge of the structures of these intermediates is therefore necessary for a full understanding of the reduction process, and a preliminary investigation has already been reported (Birch 1947).

We have now investigated the structures of some of the conjugated dienes by the direct method of Alder and Rickert (1936) which consists in a reaction with dimethyl acetylenedicarboxylate to give a dimethyl phthalate and a hydrocarbon by elimination of the bridge in the intermediate adduct, for example,

$$I \rightarrow II \rightarrow III \rightarrow IV.$$

In the present work the hydrocarbon fragment was not examined. Table 1 shows the initial 2,5-dihydroanisole (I) and the structure of the 2,3-dihydro-anisole (II) deduced from the Alder-Rickert (1937a, 1937b) reaction. The reaction proceeded very readily in each case, evolution of gas beginning in the region of 100–140 °C.

The structures of the unknown derivative from 4-methylanisole and that from 4-methoxyanisole can be deduced from the known course of the diene reaction. In the former case both methyl and methoxyl are retained. It is noteworthy that in both cases the anhydride is formed spontaneously from the acid.

The results confirm the deductions already made (Birch 1947) that it is usually the enol-ether double bond which pivots about the carbon bearing the methoxyl group. No detectable amount of product could be obtained from 2,5-dihydrotoluene, although further reduction of this can be brought about

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by reaction with sodium in liquid ammonia (Birch 1947). Evidently dehydrogenation back to the aromatic compound is dominant in the case of this hydrocarbon unless reduction of the conjugated compound occurs as it is formed. Such dehydrogenations occur with the dihydroanisoles, but much less readily (Birch 1947).

The most interesting case is that of the dihydro-derivative of 2-methylanisole. This has already (Birch 1944) been shown to consist of a mixture of preponderantly 3,6-dihydro-2-methylanisole (V) with some 2,5-dihydro-2-methylanisole (VI). The conjugation reaction was carried out on this mixture

TABLE 1

2,5-Dihydro-	2,3-Dihydro-	Derivatives	Melting Point (°C)	Literature Melting Point (°C)	References
-anisole	-anisole	3 - M e t h o x y - phthalic acid	169–170	172–173	(1), (2)
		Dimethyl ester	77–77·5	73–74	(1)
		Anhydride	160–161	160–161	(2)
-3-methylanisole	-5-methylanisole II	3 - M e t h o x y - 5 - m e t h y l - phthalic acid	200–202	200–202	(3)
		Dimethyl ester	84·5–85·5	86	
		Anhydride	167–168	167	(3), (4)
-4-methylanisole	-4-methylanisole	3 - M e t h o x y - 6 - m e t h y l - phthalic acid			
		Dimethyl ester	58–59		
		Anhydride	185–186		
-4-methoxyanisole	-4-methoxy- anisole	3,6 - Dimethoxy- phthalic acid			
		Anhydride	263–264	260–261	(5)

(1) Buehler, Powers, and Michels (1944). (2) Bentley, Robinson, and Weizmann (1907). (3) Meldrum (1911). (4) Asahina and Fujikawa (1953). (5) Perkin and Weizmann (1906).

(Birch 1947) but the product was not closely examined. The Alder-Rickert product is a hitherto unknown dimethyl methoxymethylphthalate which is probably the 4-methoxy-3-methyl derivative (IX) derived from V. It cannot have been derived from the minor constituent VI by movement of the enol-ether double bond in the manner hitherto encountered to give VII, because the product would be the known dimethyl 3-methoxy-4-methylphthalate (X) (Simonsen and Rau 1921). Reaction of the mixture of conjugated compounds with maleic anhydride gave rise to a small amount of a crystalline derivative $C_{12}H_{12}O_4$ which must have the methoxyl group at a bridge-head since it showed no enol-ether properties (cf. Birch 1947). It is most probably XI formed from VII. The bulk of the adduct was a gum which showed signs of ketonic properties

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after acid treatment, although no crystalline derivatives could be obtained. The formation of such an adduct would require the presence of a 2- rather than a 1-methoxybutadiene structure, and a compound such as VIII could be responsible. The retention to some extent of the position of the enol-ether double bond in this case may be due to its lower energy level due to hyper-
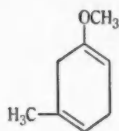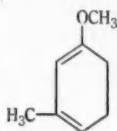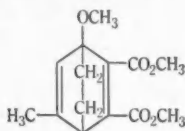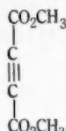
(I)   (II)   (III)
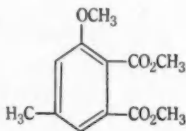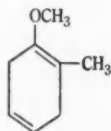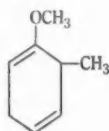
(IV)   (V)   (VI)
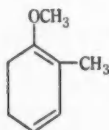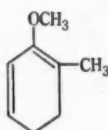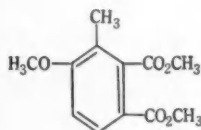
(VII)   (VIII)   (IX)
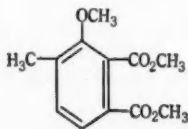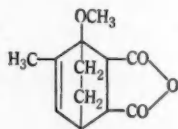
(X)   (XI)

conjugation with the methyl group. Owing to the complexity of the mixtures encountered the problem could not be further resolved, but other 2-alkylanisoles are being examined.

II. EXPERIMENTAL

(a) *Dihydroanisole Derivatives.*—These were prepared by reduction of the anisole with sodium and ethanol in liquid ammonia (Birch 1950).

(b) *Conjugation.*—The double bonds in the above were conjugated by the method of Birch (1947) using potassium amide in liquid ammonia.

(c) *Condensation with Dimethyl Acetylenedicarboxylate.*—To the 2,3-dihydroanisole derivative (2 g) was added the ester (2 g) with immediate evolution of heat and production of a greenish yellow colour. The temperature was slowly raised to 200 °C and maintained there for an hour, and the mixture then distilled, the phthalic ester coming over in the region of 130–140 °C/1 mm. The following derivatives were obtained.

2,3-Dihydroanisole, b.p. 147–149 °C, n_D^{19} 1·4830, gave dimethyl 3-methoxyphthalate, b.p. 130–140 °C/1 mm, m.p. 77–77·5 °C (from water), hydrolysed to 3-methoxyphthalic acid, m.p. 169–170 °C (from ethyl acetate-light petroleum) (Found : C, 55·5 ; H, 4·1%. Calc. for $C_9H_8O_5$: C, 55·1 ; 4·1%), converted by acetic anhydride to 3-methoxyphthalic anhydride, m.p. 160–161 °C.

5,6-Dihydro-3-methylanisole, b.p. 167–169 °C, n_D^{19} 1·4850, gave rise to dimethyl 3-methoxy-5-methylphthalate, b.p. 140–150 °C/1 mm, m.p. 84·5–85·5 °C (from water), and hence to 3-methoxy-5-methylphthalic acid, m.p. 200–202 °C (acetone) (Found : C, 57·7 ; H, 4·7%. Calc. for $C_{10}H_{10}O_5$: C, 57·1 ; H, 4·7%), and 3-methoxy-5-methylphthalic anhydride, m.p. 167–168 °C (from acetic anhydride).

2,3-Dihydro-4-methylanisole, b.p. 168–170 °C, n_D^{19} 1·4817, gave rise to dimethyl 3-methoxy-6-methylphthalate, b.p. 160–170 °C/1 mm, m.p. 58–59 °C (from water), and hence to 3-methoxy-6-methylphthalic anhydride, m.p. 185–186 °C (Found : C, 63·0 ; H, 4·1%. Calc. for $C_{10}H_8O_4$: C, 63·5 ; H, 4·2%).

2,3-Dihydro-1,4-dimethoxybenzene, b.p. 120–124 °C/30 mm, λ_{max}. 275 mμ, ε_{max}. 3160, gave rise to 3,6-dimethoxyphthalic anhydride as pale yellow prisms from acetone, m.p. 263–264 °C. The phthalic acid changed spontaneously into anhydride.

The product of the conjugation reaction on the reduction product of 2-methylanisole had b.p. 164–166 °C, n_D^{19} 14870. The Alder-Rickert reaction gave rise to a non-crystalline ester, b.p. 135–145 °C/1 mm, hydrolysed to what is probably 4-methoxy-3-methylphthalic acid, m.p. 172–173 °C (Found : C, 56·9 ; H, 4·6%. Calc. for $C_{10}H_{10}O_5$: C, 57·1 ; H, 4·8%). The anhydride formed colourless needles, m.p. 160–161 °C.

Reaction of the above conjugated compound (2 g) with maleic anhydride (3 g) in acetone (15 c.c.) occurred with development of a greenish yellow colour. After 6 hr the solvent and material boiling below 100 °C/1 mm, were removed. The residue could not be induced to crystallize, but after alkaline hydrolysis and acidification a gum was obtained, which crystallized in contact with methanol to give a solid, m.p. 139·5–140 °C (Found : C, 65·0 ; H, 6·3%. Calc. for $C_{13}H_{14}O_4$: C, 64·9 ; H, 6·3%). This gave no reaction with 2,4-dinitrophenylhydrazine. The gummy material in the mother liquor reacted with 2,4-dinitrophenylhydrazine to an orange gum which could not be crystallized.

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THE CHEMISTRY OF GLYOXALINE, PYRROLE, AND PYRAZOLE

By R. D. Brown*

Summary

The results of a study of glyoxaline, pyrrole, and pyrazole by the molecular-orbital method are reported. The theoretical data provide a detailed interpretation of the observed course of electrophilic substitutions in these heterocycles. Unequivocal predictions of the orientations for nucleophilic and radical substitutions in these compounds also emerge, but at present no relevant experimental information is available, with the exception of a possible case of radical substitution in glyoxaline.

The present study also indicates that in conjugated systems, the electronegativity of a nitrogen atom carrying a formal negative charge (or a formal negative half-electronic charge) is appreciably less than that of a neutral carbon atom. This should assist in the assignment of electronegativity parameters in future molecular-orbital calculations.

I. Introduction

The present investigation was undertaken to determine whether the simple molecular-orbital treatment of organic reactions (Brown 1952) is reliable for the smaller heterocyclic nitrogen compounds. It should also serve as a basis for interpreting future experimental studies of these compounds. They have received theoretical attention previously by Wheland and Pauling (1935) and Longuet-Higgins and Coulson (1947), who considered briefly the π-electron densities in pyrrole, and by Orgel *et al.* (1951), who reported π-electron densities for all three compounds. However, these workers did not consider localization energies and only a brief comparison with the known chemistry of the compounds was made. These last points are dealt with in detail here, and the present electron density results differ from those of previous authors owing to a somewhat different handling of the theoretical parameters relating to nitrogen atoms.

II. Method

The simple molecular-orbital method, neglecting overlap, was used to calculate atom localization energies A, for electrophilic, nucleophilic, and radical substitution, π-electron densities q, and free valences F. Relevant details of the method and the significance of A, q, and F have been discussed fully by Brown (1952). The two nitrogen atoms in pyrazole and glyoxaline were treated as equivalent; this assumption seems the more reasonable since it has been demonstrated that in pyrrole the nitrogen is hybridized sp^2 (Wilcox and Goldstein 1952), and this is doubtless also the case for the secondary nitrogens of the other two heterocycles. The major factor determining the relative π-electron densities and relative reactivities of the various ring carbon atoms is evidently the

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difference in electronegativity of N and C, so the above theoretical quantities were computed for varying values of the " relative electronegativity parameter " h, defined by

$$h = \frac{\alpha_N - \alpha_C}{\beta},$$

α_N and α_C being the Coulomb integrals* of nitrogen and carbon respectively, and β being the standard resonance integral.* Since the localization energies were found to be smooth functions of h and the same feature would therefore be expected for the charge densities and free valences, two values, $+1$ and -1, were selected to represent typical positive and negative values of h for the calculation of q and F. Values of any one of the theoretical quantities for different positions, of course, become equal at $h=0$, so that the qualitative results depend merely on the sign of h. The customary assumption was made that all carbon-carbon bonds have standard resonance integrals β, and the same values were assumed for the resonance integrals of the carbon-nitrogen and nitrogen-nitrogen bonds.

III. Results and Discussion
(a) Glyoxaline

The theoretical results for this compound are presented in Figures 1 and 4. The results applying to electrophilic substitution are of particular interest. For positive h, that is, for N more electronegative than C, as would be the case in the free glyoxaline molecule or its protonated cation, both the π-electron densities
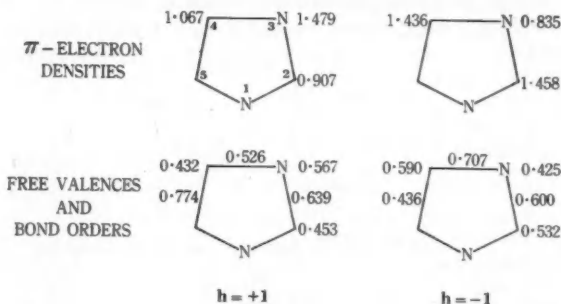
Fig. 1.—Glyoxaline : electron densities, bond orders, and free valences.

and the electrophilic localization energies imply a higher reactivity for the 4- (or tautomerically equivalent 5-) position than for the 2-position. This agrees with the observations that nitration (Rung and Behrend 1892 ; Behrend and Schmitz 1893 ; Fargher and Pyman 1919), sulphonation (Pyman and Ravald 1920 ; Barnes and Pyman 1927), and bromination (Balaban and Pyman 1922) take place at the 4-position. For negative h, however, the two alternative

* The significance of these quantities is discussed by Brown (1952).

approximations disagree.   The charge densities indicate that the 2-position
is the more reactive of the carbon atoms, while the localization energies require
the 4-position still to be the more reactive.   It has recently been demonstrated
experimentally (Brown *et al*. 1953) that diazonium coupling in glyoxaline occurs
by an electrophilic substitution of the diazonium cation in the glyoxalinate
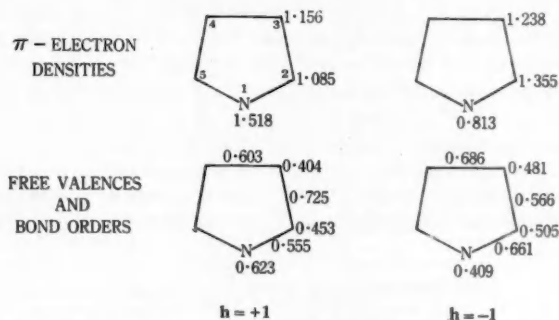anion.   Furthermore the coupling occurs preferentially at the 2-position (Fargher

Fig. 2.—Pyrrole : electron densities, bond orders, and free valences.

and Pyman 1919).   Taken together, these theoretical and experimental results
lead to several interesting conclusions.   Firstly, the localization energies cannot
be made to agree with the observed relative reactivities for any choice of h,
whereas the charge densities can be made to do so for negative h.   Thus the
π-electron potential energy curves for the 2- and 4-positions must cross over
between the activated complex and the completely localized systems (see detailed
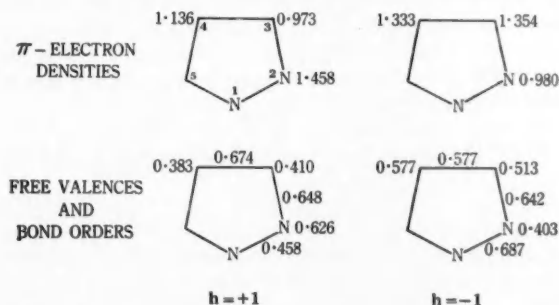
Fig. 3.—Pyrazole : electron densities, bond orders, and free valences.

discussions of energy curves by Brown 1952).   Secondly, the electron densities
agree with the observed orientation only for negative h, indicating that the
formal negative charges on the nitrogens in the glyoxalinate anion are sufficient
to reduce the electronegativity of nitrogen to less than that of a neutral carbon
atom.   On this basis we may regard the theoretical data for negative h for the
other heterocycles as being appropriate to the corresponding anions.

The iodination of glyoxaline in alkaline solutions would also seem to proceed by a S_E2 reaction involving the glyoxalinate anion, since the substitution occurs preferentially at the 2-position (Pauly and Arauner 1928).

The attack by a nucleophilic reagent would be expected to occur in a complementary manner. The electron densities and localization energies now are in agreement. In the neutral molecule the attack would be predominantly
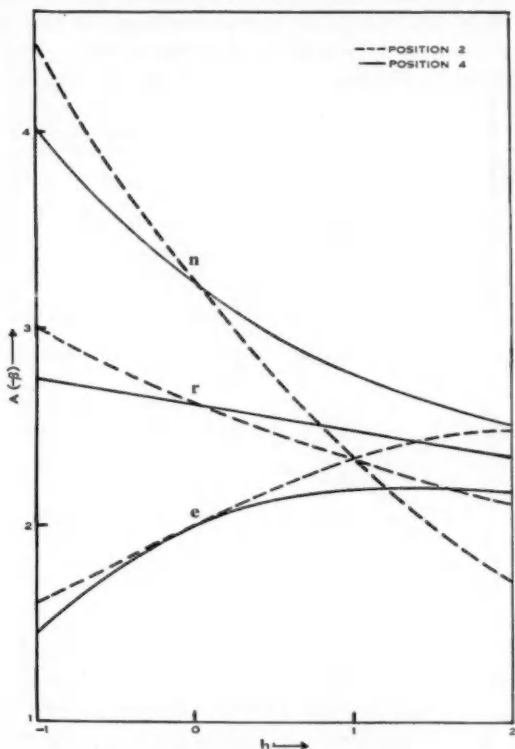
Fig. 4.—Atom-localization energies for glyoxaline. A_e, electrophilic ; A_r, radical ; A_n, nucleophilic.

at the 2-position, while the 4-position would be preferred in the anion. However, the negative charge on the latter would doubtless completely inhibit attack by the usual nucleophilic reagents.

The free valences and localization energies both point to preferential radical attack at the 2-position in the neutral molecule, and at the 4-position in the anion. There does not appear to be any clear-cut experimental evidence of the reactivity of glyoxaline towards radicals, although the reported bromination by cyanogen bromide in ether (Langenbeck 1928), in which the 2-position is preferred, might occur by attack of the uncharged molecule by bromine atoms.

(b) Pyrrole (Figs. 2 and 5)

Considering first electrophilic substitution, for positive h, that is, for N more electronegative than C, as would be the case in the free pyrrole molecule, the two extreme approximations to the π-electron activation energies disagree, the π-electron densities indicating that initially the β-position is more reactive, while it is easier to localize completely two π-electrons at the α-position than at the β-position. This means that the π-electron energy curves cross over as the electrophilic reagent approaches the pyrrole molecule, and we cannot predict which curve will be lower at the activated complex stage. Experimentally it
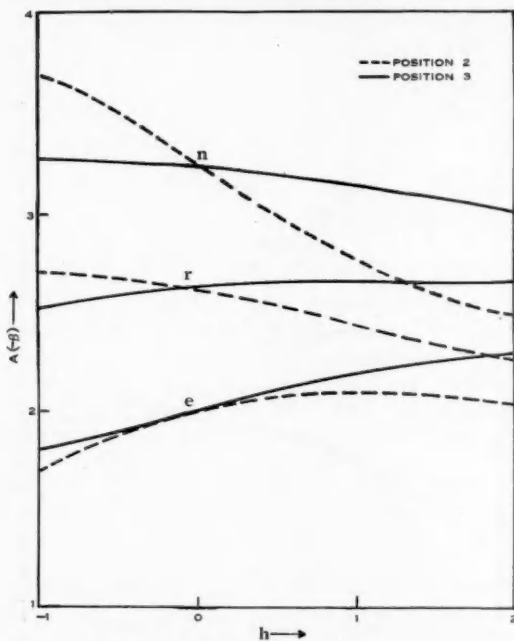
Fig. 5.—Atom-localization energies for pyrrole. A_e, electrophilic; A_r, radical; A_n, nucleophilic.

is known that the α-position is preferentially attacked by electrophilic reagents in acidic media (Fischer and Hepp 1886 ; Mazzara and Borgo 1905 ; Hess and Wissing 1914), so that the energy curves must cross before the activated complex is formed.

In alkaline solution, when pyrrole ionizes as an acid, the nitrogen carries a formal negative charge. In view of the theoretical results for glyoxaline (above), the appropriate electronegativity parameter value for the pyrrolate anion is negative. For negative h both approximations to the activation energy agree in predicting the α-position to be more reactive than the β-position towards electrophilic reagents. Experimentally it is known (Fischer and Hepp 1886)

that diazonium coupling in alkali occurs preferentially at the α-position, in agreement with the theoretical results.

For nucleophilic substitution the localization energies and charge densities agree in predicting preferential attack of the α-position in free pyrrole, and the β-position in the pyrrole anion. However, on an absolute scale the results imply that pyrrole would be very unreactive towards nucleophilic reagents, in contrast to its very high reactivity towards electrophilic reagents, so it is unlikely that reactions with the former type of reagent will be observed experimentally.
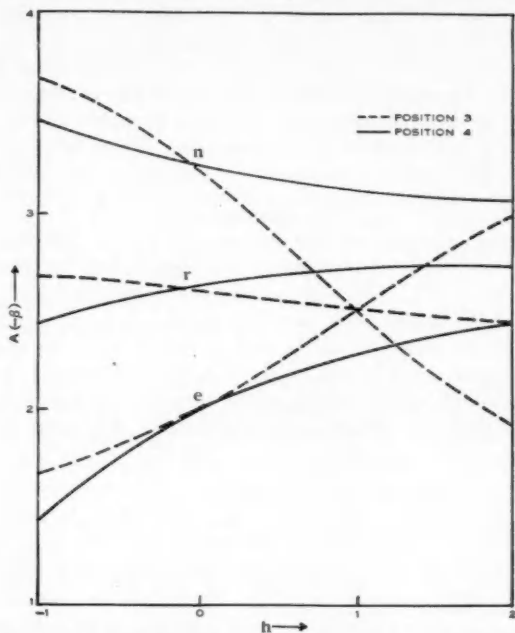
Fig. 6.—Atom-localization energies for pyrazole. A_e, electrophilic; A_r, radical; A_n, nucleophilic.

In the case of radical substitution, the localization energies and free valences both predict preferential attack of the α-position in free pyrrole, while for negative h the two approximations disagree, that is, the π-electron energy curves must cross.

(c) Pyrazole (Figs. 3 and 6)

Again let us first consider electrophilic substitution. For positive h, that is, for free pyrazole, both approximations predict preferential attack of the 4-position, and this agrees with the observations that nitration (Buchner and Fritsch 1893; Knorr 1894) and halogenation (Balbiano 1890; Knorr 1895) occur at this position. For negative h however, such as would apply to the pyrazolate anion, the localization energies indicate that the 4-position is still the more reactive, while the charge densities imply that the 3-position is more

reactive. Experimentally it has been shown (Knorr 1895) that chlorination with hypochlorite leads to 4-chloro-derivatives, and this probably occurs by electrophilic substitution in the anion, so it would seem that the localization energies lead to the correct result, that is, the energy curves cross before the transition state is reached. More detailed studies of the mechanisms of such substitution reactions in pyrazole would be valuable in this connection.

For nucleophilic substitution the two approximations are consistent, predicting the 3-position to be more reactive in free pyrazole, and the 4-position in the anion. The absolute values of the theoretical quantities imply that pyrazole would be much more reactive than pyrrole towards nucleophilic reagents, and it may prove possible to observe such substitutions in the free base.

Both the localization energies and the free valences indicate that radical substitution would occur at the 3-position in free pyrazole, and at the 4-position in the anion. Again there does not appear to be any experimental evidence on this type of substitution.

IV. CONCLUSION

From the preceding discussion it emerges that at present there is no direct disagreement between the molecular-orbital calculations and the orientations observed experimentally. However, a stringent test of the theory is not always possible because the substitution reactions of these heterocycles have not been studied in sufficient detail. The theoretical results point to some interesting lines of investigation, such as the course of radical substitution in both neutral and strongly alkaline media, which would throw more light on the question of the reliability of the simple molecular-orbital treatment of heterocyclic systems.

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COLOURING MATTERS OF AUSTRALIAN PLANTS

IV. HAEMOCORIN : A UNIQUE GLYCOSIDE FROM *HAEMODORUM CORYMBOSUM* VAHL.

By R. G. Cooke* and W. Segal*

Summary

The bulbous roots of *Haemodorum corymbosum* Vahl. yield a red crystalline glycoside, haemocorin, which is readily hydrolysed to cellobiose and the purple-red aglycone, $C_{20}H_{14}O_4$. The latter contains one methoxyl group and gives a diacetate and isomeric mono- and dimethyl ethers. The absorption spectra and other properties of these compounds suggest a polycyclic tautomeric enolone structure. Oxidation of a dimethyl ether gives a compound $C_{22}H_{18}O_7$, believed to be a lactol ester, and a compound $C_{20}H_{14}O_5$, which is apparently a polycyclic aromatic anhydride. These results indicate that the aglycone is a polycyclic enolic α-diketone, possibly of the indandione type.

I. INTRODUCTION

The family Haemodoraceae is predominantly Australian and seems to be confined almost entirely to the southern hemisphere. The genus *Haemodorum* is apparently found only in Australia, where it is represented by about 17 species. The plants have been used medicinally by the aborigines, and the bulbous roots, although acrid and bitter when raw, were roasted and used for food (Webb 1948). The roots of all species contain bright red colouring matter which has earned the popular name " blood root " for these plants.

Haemodorum corymbosum Vahl. (*H. coccineum* R.Br.) is distributed over northern Australia and is common in north Queensland. It is reputed to be toxic to livestock. When freshly broken, the bulbous roots are bright red, but the colour darkens on exposure or when the roots are dried.

II. ISOLATION OF THE COLOURING MATTER

Preliminary small-scale extractions indicated that the pigment must be a glycoside, and acid hydrolysis of the extracts readily gave the crude crystalline aglycone. Eventually a process was evolved for the isolation of a considerable proportion of the glycoside as a red crystalline solid and the remainder of the colouring matter was recovered as the aglycone.

The glycoside, now named haemocorin, separates from water as a hydrate. Even after prolonged drying, its composition is best represented as $C_{32}H_{34}O_{14}.H_2O$. It is weakly acidic and dissolves in caustic alkali with a violet colour.

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III. Identification of the Sugar

Comparison of the analyses and properties of haemocorin and its aglycone, together with quantitative determination of the amount of insoluble aglycone produced by hydrolysis, indicated that the sugar must be a C_{12} disaccharide. As haemocorin is very readily hydrolysed with very dilute acid it seemed possible that the disaccharide might be isolated intact. This was readily accomplished and the product was identified as cellobiose by melting point, rotation, paper chromatography, and the preparation of the two epimeric octa-acetates. This appears to be the first recorded natural occurrence of cellobiose as an isolated carbohydrate unit.

The steric arrangement of the glycosidic link in the pigment has not been determined.

IV. The Aglycone and Its Derivatives

The dark purple-red aglycone has the composition $C_{20}H_{14}O_4$ and contains one methoxyl group. It forms a diacetate but methylation can be controlled to give two monomethyl ethers or two corresponding dimethyl ethers. These results and the colour reactions suggest an unsymmetrical tautomeric enolone system. No carbonyl derivatives are obtainable, but infra-red analysis of a dimethyl ether shows a band at 1635 cm^{-1}, clearly due to a conjugated ketone.

Other natural colouring matters with this structural feature are curcumin, haematein, and purpurogallin, but the occurrence of tautomerism has not been established for these. As the colour reactions and some other properties of the last two show some similarity to those of the new colouring matter, a detailed comparison of absorption spectra has been made. The results are shown in Table 1.

The ultraviolet absorption of the aglycone is similar to that of purpurogallin, and two maxima near 355 and 375 mμ seem to be common to other tropolones. The formation of isomeric ethers with infra-red carbonyl absorption at about 1630 cm^{-1} is also characteristic of some tropolones (e.g. β-methyltropolone). The infra-red absorption spectra of the two aglycone monomethyl ethers show bands which are claimed to be characteristic of the tropolone structure (Scott and Tarbell 1950 ; Cook and Loudon 1951). In particular, monomethyl ether B (in " Nujol ") shows a broad hydroxyl band at 3200 cm^{-1} and a carbonyl band at 1620 cm^{-1}. However, these results are evidently due to intermolecular hydrogen bonding because in chloroform solution a sharp hydroxyl band is found at 3519 cm^{-1}. The monomethyl ether A shows a rather broad hydroxyl band at 3387 cm^{-1} in chloroform, little different from the value for the solid. This compound therefore has some degree of internal hydrogen bonding and this is compatible with its lower melting point, lower solubility in alcohol, and its extraction from alkaline solution by chloroform. An enolic α-dicarbonyl structure therefore seems possible for this ether, but the locations of the hydroxyl and carbonyl bands in the infra-red spectrum do not support the tropolone structure.

The resemblance of the aglycone to purpurogallin is also superficial. Thorn and Barclay (1952) have shown that alkylation and acylation of purpurogallin

cause extensive changes in the light absorption. However, the new colouring matter and its derivatives all have similar spectra. Furthermore, the blue colour of an alkaline solution of purpurogallin is due to oxidation and is discharged by dithionite. The blue colour of alkaline solutions of the aglycone is due to

TABLE 1

ABSORPTION SPECTRA

Italicized figures represent inflexions

Purpurogallin						
$\lambda_{max.}$ (mμ)	245	280	305	357·5	375	432·5
log $\varepsilon_{max.}$	4·08	4·37	4·48	3·70	3·69	3·47
Aglycone						
$\lambda_{max.}$ (mμ)	250	277·5	*300*	355	372·5	505
log $\varepsilon_{max.}$	4·20	4·36	*4·23*	3·72	3·72	3·71
Monomethyl ether *A*						
$\lambda_{max.}$ (mμ)	*252·5*	275	*300*	357·5	373·5	475
log $\varepsilon_{max.}$	*4·26*	4·35	*4·18*	3·83	3·90	3·73
Monomethyl ether *B*						
$\lambda_{max.}$ (mμ)	247·5	280	—	353·5	370	455
log $\varepsilon_{max.}$	4·11	4·27	—	3·96	4·00	3·94
Dimethyl ether *A**						
$\lambda_{max.}$ (mμ)	*250*	275	*297·5*	*357·5*	372·5	467·5
log $\varepsilon_{max.}$	*4·20*	4·37	*4·13*	*3·81*	3·93	3·78
Dimethyl ether *B**						
$\lambda_{max.}$ (mμ)	—	280	—	*362·5*	372·5	475
log $\varepsilon_{max.}$	—	4·33	—	*3·94*	4·00	3·94
Diacetate						
$\lambda_{max.}$ (mμ)	—	267·5	—	*352·5*	365	430
log $\varepsilon_{max.}$	—	4·42	—	*3·92*	4·09	3·85
Haematein						
$\lambda_{max.}$ (mμ)	277·5	295	308·5	—	—	430
log $\varepsilon_{max.}$	3·86	3·51	3·46	—	—	4·60
Curcumin						
$\lambda_{max.}$ (mμ)	265	—	—	—	—	420
log $\varepsilon_{max.}$	4·18	—	—	—	—	4·77

* Measured in 95% ethanol, all others in dioxan.

the anion and it is preserved by dithionite. Finally, none of the rearrangements or substitutions characteristic of tropolones has been obtained with derivatives of haemocorin.

The absorption spectra of the new compounds do suggest a polycyclic aromatic structure.

V. OXIDATION PRODUCTS

Oxidation of dimethyl ether A, $C_{22}H_{18}O_4$, with permanganate in acetone gives two products. One of these is a neutral yellow compound $C_{20}H_{14}O_5$ containing two methoxyl groups. It slowly dissolves on heating with aqueous alkali and is recovered on acidification—the initially light coloured precipitate rapidly becoming yellow. The infra-red spectrum (in " Nujol ") shows bands at 1764 and 1727 cm^{-1}, indicating a conjugated anhydride. This is confirmed by conversion to a colourless dimethyl ester from which the anhydride is readily recovered by alkaline hydrolysis followed by acidification. The properties of this compound are very similar to those of many known polycyclic aromatic anhydrides.

The other oxidation product has the composition $C_{22}H_{18}O_7$ with three methoxyl groups. It dissolves readily in cold dilute alkali, and is recovered on acidification, but it is not attacked by diazomethane. On hydrolysis with alkali it gives an acid $C_{21}H_{16}O_7$ (two methoxyls) which reacts with diazomethane to give a product $C_{23}H_{20}O_7$ (four methoxyls). The latter is also obtained when the alkaline solution of the compound $C_{22}H_{18}O_7$ is carefully neutralized and the precipitate is rapidly recovered and treated with diazomethane. When boiled with sodium hydroxide and then oxidized with silver oxide, the compound $C_{22}H_{18}O_7$ is converted to the yellow anhydride $C_{20}H_{14}O_5$.

These changes suggest that the oxidation of the aglycone dimethyl ether may be interpreted by the following part structures :
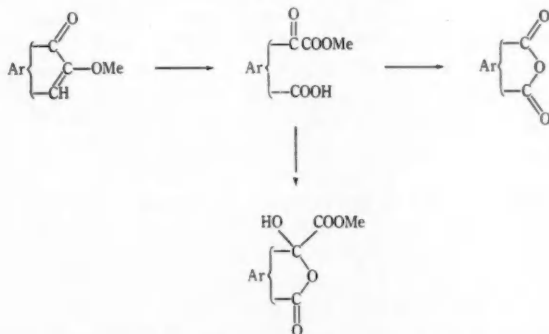
It therefore seems probable that the aglycone is a polycyclic enolic α-diketone, perhaps of the indandione type. The compound also seems to have an extended enolone system involving more than one ring and possibly analogous to that in haematein.

VI. EXPERIMENTAL

Unless otherwise stated, all melting points are corrected and were observed in Pyrex capillaries. Light petroleum refers to a fraction of boiling range 40–60 °C. Microanalyses are by Dr. K. W. Zimmermann and assistants.

(a) *Extraction of the Colouring Matter.*—The fresh roots were separated as far as possible from fibrous rootlets and from adhering sand. They were then sliced and steeped in cold methanol,

the extract being removed at intervals and replaced with fresh solvent until the material was exhausted.   The deep crimson extract was then evaporated in stages and any material deposited was removed by filtration or decantation.   This material was usually resinous in appearance, but a granular red solid was sometimes deposited in the later stages.   Finally, when nearly all the methanol had been removed, water was added to the syrup, the remainder of the methanol was evaporated under reduced pressure, and the aqueous solution was shaken with ether.   On standing, much of the glycoside was deposited as crystals.   These were filtered and the filtrate was further concentrated under reduced pressure and the process repeated until no more glycoside could be obtained.   Glycoside was also extracted from the resinous deposits (above) by heating repeatedly with water and decanting the hot solution.   Finally, extraction of the dried resinous residue with hot benzene gave considerable quantities of the aglycone.   Acid hydrolysis of the final aqueous filtrates gave more of the aglycone.   The total yield of colouring matter was as high as $0 \cdot 3\%$ (expressed as aglycone from dried roots).

(*b*) *Haemocorin.*—The crude glycoside was crystallized repeatedly from hot water and *haemocorin* separated in glistening red spangles with a bronze lustre.   For analysis a sample was further crystallized from absolute ethanol and dried in a vacuum at 100 °C for 2 days, m.p. 263–264 °C (decomp. uncorr.) (Found : C, $58 \cdot 0$; H, $5 \cdot 9\%$.   Calc. for $C_{32}H_{34}O_{14}.H_2O$: C, $58 \cdot 2$; H, $5 \cdot 5\%$).   Pure haemocorin is readily soluble in hot water but almost insoluble in the cold. It dissolves readily in dilute aqueous sodium hydroxide with a stable violet colour.

(*c*) *Hydrolysis of Haemocorin.*—In small-scale quantitative experiments the glycoside $(0 \cdot 1 – 0 \cdot 15$ g) was dissolved in water (70 c.c.) by heating on the water-bath.   Concentrated hydrochloric acid (2 drops) was then added and the heating was continued for 30–45 min.   The cooled mixture was allowed to stand until the crystalline aglycone was completely precipitated and the liquid was almost colourless.   The colouring matter was then collected, washed with water, and dried to constant weight.   The average yield was about 47% of the weight of glycoside. The combined filtrates from several experiments were neutralized with lead carbonate, filtered, and evaporated to dryness under reduced pressure.   The sugar was extracted from the residue with hot absolute ethanol.   In a typical larger-scale experiment the glycoside (3 g) was dissolved in hot water (500 c.c.) and sulphuric acid ($0 \cdot 5$ c.c.) was added.   The mixture was heated on the water-bath for 1 hr and the crystalline precipitate of aglycone was recovered, washed, and dried. Yield $1 \cdot 3$ g.

(*d*) *Identification of the Sugar.*—Concentration of the alcoholic extracts (above) gave a microcrystalline powder, m.p. 224–225 °C (decomp. uncorr.) and $[\alpha]_D^{20}$ $+34 \pm 0 \cdot 7°$ (*c*, $1 \cdot 5$ in water).   The literature gives m.p. 225 °C for β-cellobiose and $[\alpha]_D$ $+34 \cdot 6°$ (*c*, 8 in water).   Paper chromatography beside authentic cellobiose, gave R_F $0 \cdot 35$ in the two solvent systems, collidine-water and phenol-water (1% $NH_3 + HCN$).

The β-octa-acetate was prepared by heating for $2\frac{1}{2}$ hr with acetic anhydride and anhydrous sodium acetate.   It crystallized from absolute ethanol in fine silky needles, m.p. 196–197 °C (uncorr.) not depressed by mixing with a sample similarly prepared from authentic α-cellobiose (Found : C, $49 \cdot 5$; H, $5 \cdot 8\%$.   Calc. for $C_{26}H_{36}O_{19}$: C, $49 \cdot 6$; H, $5 \cdot 6\%$).

The α-octa-acetate was prepared by heating the sugar or the above β-octa-acetate with acetic anhydride and a trace of sulphuric acid.   It crystallized from absolute ethanol in short needles, m.p. 225–226 °C (uncorr.) not depressed by mixing with authentic material (Found : C, $49 \cdot 6$; H, $5 \cdot 8\%$.   Calc. for $C_{26}H_{36}O_{19}$: C, $49 \cdot 6$; H, $5 \cdot 6\%$).

(*e*) *The Aglycone.*—The crude hydrolysis product was crystallized repeatedly from acetone, sublimed in a high vacuum, and again crystallized from acetone.   The *aglycone* formed dark purple-red plates, or almost black needles with a bronze lustre, m.p. 277–278 °C (decomp.) (Found : C, $75 \cdot 3$; H, $4 \cdot 4$; O, $20 \cdot 5$; MeO, $9 \cdot 6\%$.   Calc. for $C_{20}H_{14}O_4$: C, $75 \cdot 5$; H, $4 \cdot 4$; O, $20 \cdot 1$; $1 \times MeO$, $9 \cdot 7\%$).

The compound is moderately soluble in ethanol or acetone and sparingly soluble in benzene, giving purple-red solutions.   It dissolves in concentrated sulphuric acid with an emerald-green colour, and in aqueous alkalis it gives a transient blue colour which changes to green, and finally yellow or brown.   These changes are due to oxidation and the blue colour can be preserved by

the addition of dithionite.   Even tap-water produces the blue colour if added to the red solutions in ethanol or acetone.   The alkaline solutions also exhibit an intense blue fluorescence in daylight.

The *diacetate* was prepared by treatment with acetic anhydride and pyridine.   It crystallized from acetone as orange needles, m.p. 248 °C (Found : C, 71·7 ; H, 4·5 ; O, 24·0 ; MeO, 7·8%. Calc. for $C_{24}H_{18}O_6$: C, 71·6 ; H, 4·5 ; O, 23·9 ; $1 \times$ MeO, 7·7%).

(*f*) *Preparation of Monomethyl Ethers.*—The aglycone (1·3 g) was refluxed in dry acetone (200 c.c.) with dimethyl sulphate (1·5 g) and excess of sodium bicarbonate.   After about 48 hours' heating, the acetone was evaporated and the residue treated with aqueous sodium hydroxide.   Most of the product dissolved and the mixture was then shaken with ether.   The deep violet alkaline solution was separated and acidified to give a mixture of the crude mono-methyl ethers.   The dried product (0·9 g) was dissolved in acetone and passed over a column of magnesium carbonate.   One fraction readily passed through the column and another was firmly held as a violet band.   A small amount of unchanged aglycone formed a narrow blue band at the top of the column.

The violet band was removed and the magnesium carbonate was dissolved with dilute hydrochloric acid.   The undissolved solid was recovered and crystallized from ethanol, giving *monomethyl ether A* as purple-red prisms, m.p. 212–214 °C (Found : C, 76·0 ; H, 5·0 ; MeO, 18·7%.   Calc. for $C_{21}H_{16}O_4$: C, 75·9 ; H, 4·9 ; $2 \times$ MeO, 18·7%).   This compound is sparingly soluble in ethanol.   It dissolves slowly in dilute sodium hydroxide with a violet colour ; con-centrated alkali precipitates the salt.   It is extracted from alkaline solution by chloroform. Attempts to prepare a copper derivative were unsuccessful.   The infra-red spectrum (in " Nujol ") has bands at 3378, 1656, 1609, 1584, 1554, 1498, 1319, 1295, 1273, 1238, 1214, 1182, and 1166 cm⁻¹.

The *acetate* crystallized from ethanol in orange leaflets, m.p. 223 °C (Found : C, 73·6 ; H, 4·9%.   Calc. for $C_{23}H_{18}O_5$: C, 73·8 ; H, 4·8%).

The acetone eluate from the magnesium carbonate column was evaporated and the residue was crystallized from ethanol or aqueous acetone to obtain *monomethyl ether B* as red plates, m.p. 259 °C (Found : C, 75·9 ; H, 5·1 ; MeO, 18·4%.   Calc. for $C_{21}H_{16}O_4$: C, 75·9 ; H, 4·9 ; $2 \times$ MeO, 18·7%).   This compound is more soluble in ethanol than the isomer.   It is readily soluble in aqueous sodium hydroxide with a violet colour and is not extracted from alkaline solution with chloroform.   The infra-red spectrum (in " Nujol ") has bands at 3200, 1620, 1607, 1589, 1568, 1553, 1513, 1493, 1332, 1316, 1308, 1293, 1276, 1228, 1185, and 1171 cm⁻¹.

(*g*) *Preparation of Dimethyl Ethers.*—The aglycone was methylated by refluxing with excess dimethyl sulphate and potassium carbonate in acetone, usually with addition of a little dithionite and under a nitrogen atmosphere.   When the initially purple solution had become orange, the acetone was nearly all evaporated and the residue was stirred with aqueous sodium hydroxide to hydrolyse any dimethyl sulphate.   The fully methylated material was then extracted with ether, the extracts being well washed with dilute aqueous sodium hydroxide and then with water. When monomethyl ether was present in the alkaline washings it was recovered by acidification.

The fully methylated product was recovered from the dried ethereal solution and the two isomers were separated by chromatography of a benzene solution on alumina.

The first product eluted—*dimethyl ether A*—was crystallized from ether as orange plates or prisms, and from benzene-light petroleum as large orange-red prisms, m.p. 172–173 °C (Found : C, 76·0 ; H, 5·4 ; MeO, 26·7% ; mol. wt., 362.   Calc. for $C_{22}H_{18}O_4$: C, 76·3 ; H, 5·2 ; $3 \times$ MeO; 26·9% ; mol. wt., 346).   This compound is also obtained by further methylation of the monomethyl ether *A*.

The *dimethyl ether B* crystallized from anhydrous ether as small orange plates or prisms, and from benzene-light petroleum as orange-red prisms, m.p. 147–148 °C (Found : C, 76·7 ; H, 5·4 ; MeO, 26·8%.   Calc. for $C_{22}H_{18}O_4$: C, 76·3 ; H, 5·2 ; $3 \times$ MeO, 26·9%).   When crystallized from *moist* ether, it separated as fine matted orange needles, apparently hydrated and having m.p. 82 °C.   This dimethyl ether was also obtained by further methylation of mono-methyl ether *B*.

No carbonyl derivatives could be obtained from these dimethyl ethers.

(*h*) *Oxidation of Dimethyl Ether A.*—The dimethyl ether (0·3 g) in purified acetone (10 c.c.) was added all at once to a cold solution of potassium permanganate (0·6 g) in purified acetone

(60 c.c.) and the total volume was made up to 80 c.c. with acetone. The mixture was kept at room temperature and shaken occasionally during 24 hr. The acetone was then removed at the pump, dilute sulphuric acid was added, and the manganese compounds were reduced with sulphur dioxide. The yellow granular solid was collected and separated into two components by fractional crystallization from ethanol, or by chromatography of a solution in benzene-ethanol over silica gel. Extraction of an ethereal solution with aqueous alkali could also be used for separation.

(i) *The Anhydride* $C_{20}H_{14}O_5$.—The material eluted first from the silica column was recrystallized from ethanol and the *anhydride* separated as yellow prisms or blades, m.p. 165–166 °C followed by solidification and remelting at 176–177 °C (Found : C, 71·6 ; H, 4·3 ; MeO, 18·3%. Calc. for $C_{20}H_{14}O_5$: C, 71·8 ; H, 4·2 ; 2×MeO, 18·6%). In organic solvents this compound showed a brilliant yellow-green fluorescence in daylight. It was insoluble in cold alkali but dissolved slowly on heating to give a colourless solution. On acidification, a light coloured precipitate was deposited but this rapidly turned yellow, especially on heating, and on crystallization from ethanol the anhydride was recovered (m.p. and mixed m.p.). When the cold alkaline solution was carefully neutralized and the precipitate was rapidly recovered, it proved to be an acid which reacted with diazomethane to form an *ester*. This crystallized from methanol in colourless plates or prisms, m.p. 150·5–151 °C (Found : C, 69·6 ; H, 5·0 ; MeO, 30·8%. Calc. for $C_{22}H_{20}O_6$: C, 69·5 ; H, 5·2 ; 4×MeO, 32·6%). Crystallization of the intermediate acid from ethanol gave only the yellow anhydride. Alkaline hydrolysis of the ester and acidification also reformed the anhydride (m.p. and mixed m.p.).

(j) *The Lactol Ester* $C_{22}H_{18}O_7$.—The main product from the oxidation of the dimethyl ether was a *lactol ester* which crystallized from ethanol as pale yellow plates or prisms, m.p. 256–256·5 °C (Found : C, 67·0 ; H, 4·6 ; MeO, 23·5%. Calc. for $C_{22}H_{18}O_7$: C, 67·0 ; H, 4·6 ; 3×MeO, 23·6%). Solutions of this compound have a bright blue fluorescence in daylight. The substance dissolves readily in cold dilute alkali and is regenerated by acidification, but it does not react with diazomethane. If the alkaline solution is carefully neutralized and the precipitate is rapidly recovered and immediately treated with diazomethane, an *ester* is produced. This separates from methanol as small needles, m.p. 183–183·5 °C (Found : C, 67·7 ; H, 5·0 ; MeO, 29·4%. Calc. for $C_{23}H_{20}O_7$: C, 67·6 ; H, 4·9 ; 4×MeO, 30·4%).

(i) *Hydrolysis.* The lactol ester $C_{22}H_{18}O_7$ was hydrolysed with boiling sodium hydroxide (10%) to an *acid*, which crystallized from benzene in prisms, m.p. 195·5–196·5 °C (Found : C, 66·7 ; H, 4·4 ; MeO, 16·0%. Calc. for $C_{21}H_{16}O_7$: C, 66·3 ; H, 4·2 ; 2×MeO, 16·3%).

By the action of diazomethane this acid was converted to the ester $C_{23}H_{20}O_7$ described above (m.p. and mixed m.p.).

(ii) *Oxidation.* The lactol ester (0·25 g) was heated with sodium hydroxide solution (5% ; 20 c.c.) on the water-bath for 1 hr. A solution of silver nitrate (1 g) was added and the heating was continued for about 4 hr. The hot mixture was filtered and the filtrate was acidified with hydrochloric acid. The yellow precipitate was crystallized from ethanol as small yellow needles, m.p. 165–166 °C and 176–177 °C alone or mixed with the anhydride described in Section VI (i) (Found : C, 71·5 ; H, 4·5 ; MeO, 18·9%).

VII. ACKNOWLEDGMENTS

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H

ALKALOIDS OF *EVODIA ALATA* F. MUELL.

By R. J. Gell,* G. K. Hughes,* and E. Ritchie*

Summary

From the bark of *Evodia alata* F. Muell. the known alkaloids, evoxanthine, melicopidine, and kokusaginine have been isolated.

The leaves contain evoxanthine and two new alkaloids. These are 2,3,4-trimethoxy-10-methylacridone (I, R=CH₃) and a furoquinoline alkaloid, evolatine. Evolatine is shown by degradation to be 7-(2′,3′-dihydroxy-3′-methylbutoxy)-6-methoxydictamnine (V).

I. INTRODUCTION

In recent papers (Hughes and Neill 1949 ; Cannon *et al.* 1952 ; Hughes, Neill, and Ritchie 1952 ; Eastwood, Hughes, and Ritchie 1954) investigations of the alkaloids of a Queensland rain-forest tree, *Evodia xanthoxyloides* F. Muell. have been reported. The present paper is concerned with the alkaloids of the closely related New Guinea species, *Evodia alata* F. Muell. It is also a small tree of secondary growth and its bark when freshly cut is bright yellow.

From a methanolic extract of the bark, the acridine alkaloids, evoxanthine and melicopidine, were isolated in 1 per cent. yield together with the furoquinoline alkaloid, kokusaginine in 0·1 per cent. yield.

The leaves yielded evoxanthine in 0·4 per cent. yield and two new alkaloids. The first of these, a pale yellow compound was obtained in 0·3 per cent. yield. It was identified as 2,3,4-trimethoxy-10-methylacridone (I, R=CH₃) by direct comparison with a synthetic specimen (Hughes and Ritchie 1951) and by demethylation to 4-hydroxy-2,3-dimethoxy-10-methylacridone (I, R=H). This

(I)
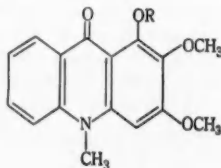
latter substance was also isolated from both the bark and leaves but is not claimed to be an alkaloid as it may have been formed by demethylation during the isolation. However, as it was obtained in much larger quantities than would be expected it is probable that the substance is actually a constituent of the leaves. It was also obtained during the isolation of the alkaloids from the

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leaves of *E. xanthoxyloides* (Hughes, Neill, and Ritchie 1952). The second new alkaloid, a colourless compound was obtained in 0·06 per cent. yield and has been named evolatine.

II. The Structure of Evolatine

Evolatine, $C_{13}H_{21}O_6N$, is an optically active, weak base, contains two methoxyl groups, and gives a negative methylenedioxy test. It is isomeric with evoxine (II) and has been degraded by reactions similar to those employed for evoxine (Eastwood, Hughes, and Ritchie 1954).
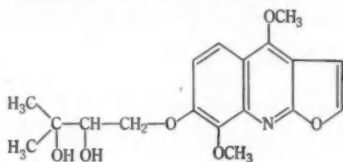
(II)

On heating with methyl iodide under pressure, evolatine is converted to optically active *iso*evolatine, a very weak base containing only one methoxyl group, which suggested that evolatine is a furoquinoline alkaloid. Supporting evidence
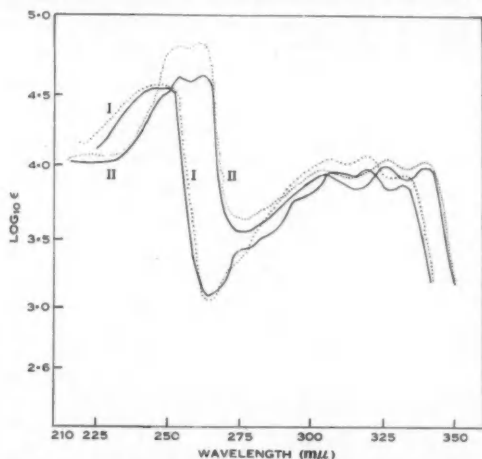
Fig. 1.—The ultraviolet absorption spectra of evolatine and *iso*evolatine and of kokusaginine and *iso*kokusaginine.

Curve I, —— Evolatine.
···· Kokusaginine.
Curve II, —— *iso*Evolatine.
···· *iso*Kokusaginine.

was obtained from ultraviolet absorption spectra of evolatine and *iso*evolatine, which, as shown in Figure 1, are almost identical with those of kokusaginine and *iso*kokusaginine respectively.

Fusion of evolatine with potassium hydroxide yielded an optically inactive phenol, $C_{13}H_{11}O_4N$, containing two methoxyl groups, which on methylation formed a base, $C_{14}H_{13}O_4N$, with three methoxyl groups, recognized as kokusaginine (III, $R = R' = CH_3$).

The phenol must therefore be III, $R = H$, $R' = CH_3$, or III, $R = CH_3$, $R' = H$. In order to decide between these the
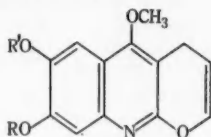

(III)

phenol was ethylated to the base $C_{15}H_{15}O_4N$, and this hydrogenolyzed in the presence of Adams's catalyst, then demethylated to the 3-ethyl-2,4-dihydroxy-quinoline, by a method similar to that used for the degradation of evolitrine (Cooke and Haynes 1954). Of the two possibilities, 7-ethoxy-3-ethyl-6-methoxy-and 6-ethoxy-3-ethyl-7-methoxy-2,4-dihydroxyquinoline, the former appeared to be more accessible, and it was first synthesized. Condensation of 3-ethoxy-4-methoxyaniline with diethyl ethyl malonate (Baker, Lappin, and Riegel 1946) in boiling diphenyl ether gave the required 7-ethoxy-3-ethyl-6-methoxy-2,4-
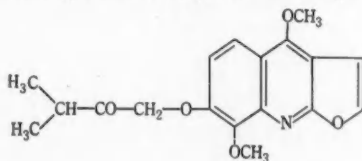
(IV)
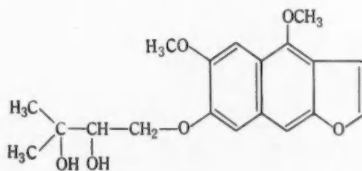
(V)

dihydroxyquinoline. This was identical with the substance obtained from the phenol as shown by direct comparison (mixed melting points) of the dihydroxyquinolines themselves and their acetyl derivatives. The phenol is therefore III, $R = H$, $R' = CH_3$.

Since both evolatine and evoxine lost a fragment of $C_5H_{10}O_2$ on potassium hydroxide fusion, it appeared that both alkaloids contained identical side-chains. As expected, evolatine absorbed 1 mole of periodic acid, and acetone was isolated

in almost quantitative yield as its-2,4-dinitrophenylhydrazone. Also evolatine underwent a pinacol-pinacolone change on heating with aqueous hydrochloric acid. The product $C_{18}H_{19}O_5N$ was isomeric with evoxoidine (IV) obtained from evoxine by the same reaction, but insufficient was available for further investigation. Evolatine is thus a 1,2-glycol and has the structure V.

III. EXPERIMENTAL

Melting points are uncorrected. Light petroleum refers to the fraction of b.p. 60–90 °C. Ultraviolet absorption spectra were measured in ethanol on a Beckman D.U. ultraviolet spectrophotometer. Analyses are by Dr. K. W. Zimmerman, C.S.I.R.O., and Miss B. Stevenson, University of Sydney.

(a) *Extraction of the Bark.*—The dry, milled bark (2·3 kg) was exhausted with methanol by cold percolation. After concentration, the brown viscous residue was repeatedly extracted with hot hydrochloric acid (5% ; 3 l.). After standing overnight, the mixture was filtered and the acid extract made alkaline with ammonia. The alkaline solution was extracted with chloroform (1·5 l.) and this concentrated to about 500 ml. After standing for several days, the yellow precipitate of almost pure evoxanthine was collected and the filtrate evaporated to dryness. A small portion of the residue was dissolved in ether, and the solution saturated with hydrogen chloride. The orange precipitate of melicopidine hydrochloride was collected and the free base liberated with ammonia. In this way a small quantity of pure melicopidine could be obtained but the process was not satisfactory if carried out on a large scale. The main bulk of the residue was heated under reflux with ethanol (200 ml) and concentrated hydrochloric acid (20 ml) for 2 hr. After cooling, the orange precipitate was collected and extracted with warm 2% hydrochloric acid. The residue consisting of demethylated compounds was boiled with chloroform and the insoluble *nor*evoxanthine filtered. On concentration, the mother liquors deposited orange needles of *nor*melicopidine, and evaporation of the mother liquors, followed by addition of ethanol, precipitated 4-hydroxy-2,3-dimethoxy-10-methylacridone. The 2% hydrochloric acid extract was made alkaline with ammonia and the solution exhausted with chloroform. The extract was filtered through alumina and crude kokusaginine obtained on removal of the solvent.

The yields of evoxanthine and melicopidine were approximately 1%, kokusaginine 0·1%, and 4-hydroxy-2,3-dimethoxy-10-methylacridone 0·05%.

(b) *Evoxanthine.*—Evoxanthine crystallized from ethanol in pale yellow cubes, m.p. and mixed m.p. with an authentic specimen 217–218 °C (Found : C, 68·1 ; H, 4·8%. Calc. for $C_{16}H_{13}O_4N$: C, 67·8 ; H, 4·6%).

Demethylation with ethanolic hydrochloric acid afforded *nor*evoxanthine which crystallized from dioxan in orange needles, m.p. and mixed m.p. 274–275 °C.

(c) *Melicopidine.*—Melicopidine crystallized from methanol in yellow prisms, m.p. and mixed m.p. with an authentic specimen 121–122 °C (Found : C, 65·5 ; H, 5·0%. Calc. for $C_{17}H_{15}O_5N$: C, 65·2 ; H, 4·8%).

Demethylation with ethanolic hydrochloric acid afforded *nor*melicopidine which crystallized from chloroform in orange needles, m.p. and mixed m.p. 208–209 °C.

(d) *Kokusaginine.*—Kokusaginine crystallized from ethanol in colourless needles, m.p. and mixed m.p. with an authentic specimen 170–171 °C (Found : C, 64·9 ; H, 5·3%. Calc. for $C_{14}H_{13}O_4N$: C, 64·9 ; H, 5·1%).

The picrate crystallized from methanol in fine yellow needles, m.p. and mixed m.p. 217–218 °C.

Treatment with methyl iodide at 100 °C under pressure yielded *iso*kokusaginine as colourless needles from ethanol, m.p. and mixed m.p. 247–248 °C.

(e) *4-Hydroxy-2,3-dimethoxy-10-methylacridone.*—The substance crystallized from ethanol in golden yellow needles, m.p. and mixed m.p. 176–177 °C.

(f) *Extraction of the Leaves.*—The dry, milled leaves (11 kg) were exhausted by cold percolation with methanol. After concentration, the residue was repeatedly extracted with hot hydro-

chloric acid (5% ; 5 l.). The mixture was filtered from black tarry matter and the acid solution made alkaline with ammonia. The alkaline solution was exhausted with chloroform and this concentrated to about 1 l. After standing for several days, a pale yellow precipitate of almost pure evoxanthine was collected and the filtrate extracted with 1% hydrochloric acid until no further precipitate was obtained on basification. The residual chloroform solution C was retained and the combined acid extracts made alkaline with ammonia. The alkaline solution was exhausted with chloroform and this passed through a short column of alumina. Removal of the solvent left a white residue consisting of crude evolatine. The chloroform solution C was evaporated to dryness and the residue dissolved in hot ethanol (300 ml). After standing for several days, the orange precipitate of 4-hydroxy-2,3-dimethoxy-10-methylacridone which separated was collected and the filtrate concentrated to about 50 ml. After standing for a further period, a yellow solid separated. This consisted of crude 2,3,4-trimethoxy-10-methylacridone and traces of evoxanthine.

The yield of evoxanthine was 0·4%, 2,3,4-trimethoxy-10-methylacridone and its demethylation product 0·3%, and evolatine 0·06%.

(*g*) *2,3,4-Trimethoxy-10-methylacridone.*—It crystallized from benzene-light petroleum in pale yellow prisms, m.p. and mixed m.p. with an authentic specimen 169–170 °C (Found : C, 68·6 ; H, 5·7%. Calc. for $C_{17}H_{17}O_4N$: C, 68·3 ; H, 5·7%).

Demethylation with ethanolic hydrochloric acid afforded 4-hydroxy-2,3-dimethoxy-10-methylacridone which crystallized from ethanol in golden-yellow needles, m.p. and mixed m.p. 176–177 °C.

(*h*) *Evolatine.*—Evolatine crystallized from acetone in glistening colourless needles, m.p. 201–202 °C (Found : C, 62·2 ; H, 6·3 ; N, 4·1 ; O, 27·1 ; CH₃O, 18·2%. Calc. for $C_{18}H_{21}O_5N$: C, 62·3 ; H, 6·1 ; N, 4·0 ; O, 27·7 ; $2 \times CH_3O$, 17·9%) and $[\alpha]_D^{24}$ +17·5° (*c*, 0·3 in ethanol). When pure, evolatine was practically insoluble in benzene and chloroform, and moderately soluble in ethanol, methanol, ethyl acetate, and acetone. It gave a negative Labat methylenedioxy test and with concentrated sulphuric acid gave a pink colouration. Evolatine was soluble in 0·5N hydrochloric acid but insoluble in 0·1N hydrochloric acid.

(*i*) iso*Evolatine.*—Evolatine (0·5 g) and methyl iodide (5 ml) were heated in a sealed tube at 100 °C for 4 hr. The *product* (0·4 g) crystallized from methanol-benzene in colourless needles, m.p. 233–234 °C and became pink on exposure to light (Found : C, 62·3 ; H, 6·1 ; N, 4·0 ; CH₃O, 8·4%. Calc. for $C_{18}H_{21}O_5N$: C, 62·3 ; H, 6·1 ; N, 4·0 ; $1 \times CH_3O$, 8·9%) ; and $[\alpha]_D^{24}$ +29° (*c*, 0·3 in ethanol). It was insoluble in 1N hydrochloric acid and only with difficulty soluble in 2N hydrochloric acid.

(*j*) *Alkali Fusion of Evolatine.*—Evolatine (0·5 g) was added to a melt of potassium hydroxide (1 g) in water (0·4 ml) at 160 °C (bath temperature 170 °C). The mixture was stirred for 1 min, then cooled, diluted, and filtered from unreacted material. The filtrate was neutralized with acetic acid, the product extracted with chloroform, and the extract passed through a column of alumina. The *product* (0·15 g) crystallized from methanol in colourless prisms, m.p. 239–240 °C (Found : C, 63·5 ; H, 4·4 ; N, 5·4 ; OCH₃, 24·8%. Calc. for $C_{15}H_{11}O_4N$: C, 63·7 ; H, 4·5 ; N, 5·7 ; $2 \times CH_3O$, 25·3%) and $[\alpha]_D^{24}$ 0° (*c*, 0·3 in ethanol). The product was soluble in dilute hydrochloric acid, soluble in sodium hydroxide, but insoluble in sodium carbonate. It gave a faint brown colour with aqueous ethanolic ferric chloride.

(*k*) *Methylation of the Phenol III.*—The phenol (0·14 g) was methylated in the usual way with dimethyl sulphate and potassium hydroxide. The product was purified by passing its benzene solution through a column of alumina and crystallized from aqueous ethanol in colourless needles (0·023 g), m.p. and mixed m.p. with kokusaginine 170–171 °C (Found : C, 64·8 ; H, 5·0 ; CH₃O, 34·8%. Calc. for $C_{14}H_{13}O_4N$: C, 64·9 ; H, 5·0 ; $3 \times CH_3O$, 35·9%). The picrate crystallized from methanol in fine yellow needles, m.p. and mixed m.p. with kokusaginine picrate 217–218 °C.

(*l*) *Ethylation of the Phenol III.*—Ethyl iodide (0·57 g) was added to a solution of the phenol (0·9 g) and potassium hydroxide (0·21 g) in methanol (20 ml) and the mixture heated under

reflux for 3 hr. After diluting with water, the product was extracted with chloroform, and purified by passing its benzene solution through a column of alumina. The *product* ($0 \cdot 33$ g) crystallized from benzene-light petroleum then aqueous ethanol in colourless leaflets, m.p. 178–179 °C (Found : C, $65 \cdot 7$; H, $5 \cdot 5$; N, $5 \cdot 4\%$. Calc. for $C_{15}H_{15}O_4N$: C, $65 \cdot 9$; H, $5 \cdot 5$; N, $5 \cdot 1\%$).

(*m*) *Degradation of the Ethylated Phenol.*—The ethyl ether ($0 \cdot 3$ g) was dissolved in ethanol (30 ml) and hydrogenolysed at room temperature and pressure in the presence of Adams's catalyst. The product was heated under reflux with hydrochloric acid (5N ; 15 ml) for 30 min. The precipitate which separated was dissolved in aqueous sodium hydroxide (charcoal), filtered, and the product precipitated with warm acetic acid. The *product* ($0 \cdot 12$ g) crystallized from aqueous ethanol in colourless needles, m.p. 243–244 °C (Found : C, $63 \cdot 9$, H, $6 \cdot 5$; N, $5 \cdot 3\%$. Calc. for $C_{14}H_{17}O_4N$: C, $63 \cdot 9$; H, $6 \cdot 5$; N, $5 \cdot 3\%$).

(*n*) *Synthesis of 7-Ethoxy-3-ethyl-6-methoxy-2,4-dihydroxyquinoline.*—Diethyl ethyl malonate ($3 \cdot 7$ g) and 3-ethoxy-4-methoxyaniline ($3 \cdot 2$ g) in diphenyl ether (20 ml) were heated under reflux for 45 min. The mixture was cooled, hexane (50 ml) added, and the precipitate collected. The crude material was dissolved in aqueous sodium hydroxide (charcoal), the solution filtered, then the product precipitated with acetic acid. The *product* ($1 \cdot 3$ g, 25% yield) crystallized from aqueous ethanol in colourless needles, m.p. 243–244 °C (Found : C, $63 \cdot 8$; H, $6 \cdot 6$; N, $5 \cdot 6\%$. Calc. for $C_{14}H_{17}O_4N$: C, $63 \cdot 9$; H, $6 \cdot 5$; N, $5 \cdot 3\%$). The mixed m.p. with the substance obtained from (*m*) was not depressed.

The *acetyl* derivative (presumably the 4-acetoxy-) was prepared by heating the dihydroxy-quinoline ($0 \cdot 5$ g) with acetic anhydride (5 ml) and pyridine (2 drops) on the water-bath for 2 hr. After dilution with ice water, the product was isolated by means of ether, and crystallized from ethanol in colourless needles, m.p. 232–233 °C (Found : C, $62 \cdot 7$; H, $6 \cdot 3$; N, $4 \cdot 6\%$. Calc. for $C_{16}H_{19}O_5N$: C, $62 \cdot 9$; H, $6 \cdot 3$; N, $4 \cdot 6\%$).

By the same method, an acetyl derivative was prepared from the substance obtained from evolatine. It had m.p. 232–233 °C either alone or on admixture with the above (Found : C, $63 \cdot 2$; H, $6 \cdot 3$; N, $4 \cdot 6\%$. Calc. for $C_{16}H_{19}O_5N$: C, $62 \cdot 9$; H, $6 \cdot 3$; N, $4 \cdot 6\%$).

(*o*) *Periodate Oxidation of Evolatine.*—(i) Evolatine (approx. $0 \cdot 02$ g) was added to periodic acid solution ($0 \cdot 01$N ; 50 ml) and dilute sulphuric acid added until it had dissolved. After standing for the required time (see below), the solution was neutralized with saturated sodium bicarbonate, potassium iodide (20% ; 1 ml) added, and the mixture titrated with sodium arsenite solution ($0 \cdot 01$N) until the solution became light yellow. A few drops of starch indicator were added and the titration continued to the end-point. The periodic acid solution when estimated under these conditions showed no change in concentration (Found : for reaction time 3 hr, $11 \cdot 6$ ml ; for reaction time 18 hr, $12 \cdot 6$ ml. Calc. for $0 \cdot 0208$, $0 \cdot 0213$ g of $C_{18}H_{21}O_8N$: $12 \cdot 0$, $12 \cdot 3$ ml respectively). (ii) Evolatine ($0 \cdot 3$ g) was treated with periodic acid ($0 \cdot 1$N ; 50 ml) and dilute sulphuric acid added until it had dissolved. After standing for 3 hr, the mixture was distilled directly into a sulphuric acid solution of 2,4-dinitrophenylhydrazine. The precipitate was collected, washed with water, and dried at 100 °C (Found : $0 \cdot 17$ g. Calc. for acetone-2,4-dinitrophenylhydrazone : $0 \cdot 21$ g). The product was purified by passing its benzene solution through a column of alumina, and crystallized from ethanol in orange prisms, m.p. and mixed m.p. with acetone-2,4-dinitrophenylhydrazone 126–127 °C (Found : C, $45 \cdot 4$; H, $4 \cdot 2\%$. Calc. for $C_9H_{10}O_4N_4$: C, $45 \cdot 4$; H, $4 \cdot 2\%$).

(*p*) *Action of Hydrochloric Acid on Evolatine.*—A solution of evolatine ($0 \cdot 2$ g) in hydrochloric acid (20% ; 8 ml) was heated on the water-bath for 2 hr, then poured into excess aqueous potassium hydroxide. The solution was exhausted with chloroform which on evaporation left a white crystalline product. This was purified by passing its benzene solution through a column of alumina and crystallized from benzene-light petroleum and then from aqueous ethanol in colourless needles, m.p. 147–148 °C (Found : C, $65 \cdot 9$; H, $5 \cdot 8$; N, $4 \cdot 4\%$. Calc. for $C_{15}H_{19}O_5N$: C, $65 \cdot 6$; H, $5 \cdot 8$; N, $4 \cdot 3\%$).

IV. ACKNOWLEDGMENTS

The authors are indebted to Messrs. L. Womersley and L. J. Webb, C.S.I.R.O., for collection and identification of plant samples, and to Mr. K. E. Slack for some assistance in the extraction of the bark.

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THE CHEMICAL CONSTITUENTS OF AUSTRALIAN *FLINDERSIA* SPECIES

VII. THE SYNTHESIS OF DERIVATIVES OF KOKUSAGININIC AND SKIMMIANINIC ACIDS

By R. F. C. Brown*

Summary

Methylation of skimmianinic acid with diazomethane gave its methyl ester, but kokusagininic acid gave the methyl ester of 2,4,6,7-tetramethoxyquinoline-3-carboxylic acid. The synthesis of methyl skimmianinate and of methyl 2,4,6,7-tetramethoxy-quinoline-3-carboxylate is described.

I. INTRODUCTION

The determination of structure of the furoquinoline alkaloids has always involved their degradation by permanganate oxidation to the corresponding 4-methoxy-2-quinolone-3-carboxylic acids, which are then readily hydrolysed and decarboxylated to the 4-hydroxy-2-quinolones. Since the latter have very high and uncertain decomposition points, they are usually identified as their acetates, dimethyl derivatives, or 3-nitroso-derivatives, all of which are more suitable for identification. The substituted 4-hydroxy-2-quinolones required for comparison have been synthesized by the reductive cyclization of the corresponding 2-nitrobenzoylmalonic esters, followed by hydrolysis and decarboxylation to the 4-hydroxy-2-quinolone. A recent example of this general method is to be seen in the proof of the structure of the alkaloid evoxine by Eastwood, Hughes, and Ritchie (1954). Since the yield of acid in the permanganate oxidation is usually low, the overall yield of a compound suitable for identification is often as low as 5 per cent., and the method is thus restricted when only a few hundred milligrammes of the alkaloid is available. In the synthetic sequence the reductive cyclization of the 2-nitrobenzoylmalonic ester also gives unsatisfactory yields.

The synthesis of methyl dictamnate (Brown *et al.* 1954) from methylanthranilate by condensation with malonic ester to the half-amide, cyclization to 4-hydroxy-2-quinolone-3-carboxylic ester, and methylation with diazomethane suggested that the methyl esters of the acids obtained by permanganate oxidation of furoquinoline alkaloids might be more useful degradation products than the 4-hydroxy-2-quinolones. As a degradative scheme this has the advantage that only two steps are required as against three in the usual method,

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and the vigorous conditions of the hydrolysis and decarboxylation with acid are avoided.   In order to test the value of the method, the preparation and synthesis of methyl skimmianinate and methyl kokusagininate were attempted.

Skimmianine was oxidized to skimmianinic acid (Asahina and Inubuse 1930) which on brief treatment with diazomethane gave the methyl ester (Ia).

(Ia; R=CH₃)
(Ib; R=H)

(IIa; R=CH₃)
(IIb; R=H)
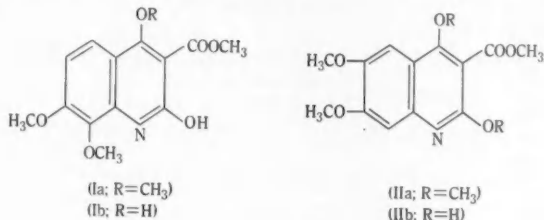
Several attempts to condense methyl 2-aminoveratrate with dimethyl malonate by heating the two substances together at 150 °C, or by refluxing in diphenyl ether, were unsuccessful, presumably because attack on the amino-group is hindered by the adjacent methoxyl and carbomethoxyl groups.   The required monoamide was finally obtained by acylating with carbomethoxyacetyl chloride and triethylamine in ether.   Cyclization of this compound with sodium methoxide yielded methyl 7,8,-dimethoxy-4-hydroxy-2-quinolone-3-carboxylate (Ib), which on brief treatment with diazomethane gave a product identical with the methyl ester of natural skimmianinic acid.   This synthesis of methyl skimmianinate provides confirmatory evidence for the linear structure of the furoquinoline ring system in skimmianine, originally assigned on the grounds of the similarity of its ultraviolet spectrum to that of dictamnine (Asahina and Inubuse 1930).   Since the final methylation is analogous to the preferential 4-methylation of 4-hydroxy-2-quinolone (Arndt, Ergener, and Kutlu 1953) methyl skimmianinate must have the structure Ia and skimmianine itself a linear ring system.

Similarly, kokusaginine was oxidized to kokusagininic acid (Terasaka 1933 ; Anet *et al.* 1952) and the acid methylated by brief treatment with diazomethane. In this case methylation proceeded further, and the product, which contained two additional methoxyl groups rather than one, must be methyl 2,4,6,7-tetra-methoxyquinoline-3-carboxylate (IIa).

Methyl 6-aminoveratrate readily condensed with dimethyl malonate at 150 °C, and the resulting monoamide was smoothly cyclized by sodium methoxide to methyl 6,7-dimethoxy-4-hydroxy-2-quinolone-3-carboxylate (IIb).   On brief treatment with diazomethane the product was methyl 2,4,6,7-tetramethoxy-quinoline-3-carboxylate, identical with that prepared from natural kokusagininic acid.   Attempts to produce monomethylation only were unsuccessful, the products being the dimethylated compound and unchanged starting material. This very ready methylation of the 2-quinolone system was unexpected in view of the effectively exclusive methylation of the 4-hydroxyl group in the synthesis of methyl skimmianinate and of methyl dictamnate (Brown *et al.* 1954).

A substance which must have been methyl 6,7-dimethoxy-4-hydroxy-2-quinolone-3-carboxylate (IIb) was first prepared by the reductive cyclization of the corresponding 2-nitrobenzoylmalonic ester by Anet *et al.* (1952), who assigned to it the isomeric structure 4-hydroxy-2,6,7-trimethoxyquinoline-3-carboxylic acid.   Its non-identity with kokusagininic acid was cited as evidence for the linear structure of the ring system in kokusaginine.   Unfortunately none of this sample was available for comparison, but there is little doubt that it was identical with the present compound IIb.   Since the present synthesis unambiguously proves its structure to be IIb, there is now no conclusive proof of the linear structure of kokusaginine.

II. Experimental

Melting points are uncorrected. Analyses are by Dr. K. W. Zimmerman, C.S.I.R.O., and by Miss B. Stevenson, University of Sydney.

(a) *Methylation of Skimmianinic Acid.*—Skimmianine (0·39 g) was oxidized with potassium permanganate in acetone as described by Asahina and Inubuse (1930), yielding skimmianinic acid (0·12 g) as colourless needles from acetic acid, m.p. 248 °C (lit. 248 °C).

Skimmianinic acid (0·12 g) suspended in methanol (25 ml) was treated with excess ethereal diazomethane at 0 °C for 5 min.   The acid rapidly dissolved and the product began to crystallize. Excess diazomethane was then destroyed with acetic acid, and the solvents were evaporated. The crystalline residue was recrystallized from methanol, giving faintly pink needles (0·08 g) of *methyl skimmianinate*, m.p. 233 °C (Found : C, 57·3 ; H, 5·2%. Calc. for $C_{14}H_{15}O_6N$: C, 57·3 ; H, 5·2%).

(b) *Acylation of Methyl 2-Aminoveratrate.*—The methyl 2-aminoveratrate was obtained by catalytic reduction of methyl 2-nitroveratrate (Pschorr and Sumuleanu 1899) and had m.p. 67 °C after crystallization from benzene-light petroleum.   Rodionov and Fedorova (1939) give m.p. 69–70 °C.

Methyl 2-aminoveratrate (1·5 g) dissolved in absolute ether (15 ml) containing anhydrous triethylamine (1 ml) was treated with a solution of carbomethoxyacetyl chloride (Staudinger and Becker 1917) (1·0 g) in absolute ether (10 ml).   The solution rapidly set to a mass of crystals which was collected, washed with water to remove triethylamine hydrochloride, and recrystallized from aqueous methanol, giving colourless needles (1·2 g) of the monoamide, m.p. 144 °C (Found : C, 54·3 ; H, 5·6%.   Calc. for $C_{14}H_{17}O_7N$: C, 54·0 ; H, 5·5%).

(c) *Methyl 7,8-Dimethoxy-4-hydroxy-2-quinolone-3-carboxylate (Ib).*—The monoamide from Section II (b) (1·0 g) dissolved in boiling absolute methanol (15 ml) was treated dropwise with a solution of sodium (0·2 g) in absolute methanol (10 ml).   The solution was heated under reflux for 1 hr, cooled and diluted with ether, and the sodium salt of the product filtered off.   The salt was decomposed with dilute acetic acid and the product crystallized from glacial acetic acid yielding fine colourless needles (0·75 g) of the *substance*, which sintered at 233 °C and charred above 320 °C (Found : C, 56·1 ; H, 4·8%.   Calc. for $C_{13}H_{13}O_6N$: C, 55·9 ; H, 4·7%).

(d) *Methyl Skiammianinate.*—The substance Ib (0·25 g) suspended in methanol (25 ml) was treated with diazomethane as described in Section II (a).   The product formed colourless needles (0·2 g) from methanol, m.p. and mixed m.p. with methyl skimmianinate prepared in Section II (a) 234 °C (Found : C, 57·2 ; H, 5·2 ; CH_3O, 41·6%.   Calc. for $C_{14}H_{15}O_6N$: C, 57·3 ; H, 5·2 ; $4 \times CH_3O$, 41·4%).

(e) *Methylation of Kokusagininic Acid.*—Kokusaginine (0·5 g) was oxidized as described by Anet *et al.* (1952), yielding kokusagininic acid (0·15 g) as an off-white powder.   The acid (0·15 g) was treated with excess diazomethane as described in Section II (a).   The crude product on recrystallization from aqueous methanol gave colourless needles (0·05 g) of methyl 2,4,6,7-tetra-methoxyquinoline-3-carboxylate, m.p. 117 °C (Found : C, 58·4 ; H, 5·3%.   Calc. for $C_{15}H_{17}O_6N$: C, 58·6 ; 5·6%).

(f) *Condensation of Methyl 6-Aminoveratrate with Dimethyl Malonate.*—Methyl 6-amino-veratrate (Arnold and Bordwell 1942) (2·1 g) and dimethyl malonate (15 ml) were heated at 150 °C for 4 hr. Excess dimethyl malonate was removed under reduced pressure, and the residue crystallized by stirring with ether. Recrystallization from methanol gave colourless leaflets (2·6 g) of the monoamide, m.p. 82–83 °C (Found : C, 54·3 ; H, 5·5%. Calc. for $C_{14}H_{17}O_7N$: C, 54·0 ; H, 5·5%).

(g) *Methyl 6,7-Dimethoxy-4-hydroxy-2-quinolone-3-carboxylate (IIb).*—The monoamide from Section II (f) (2·0 g) was cyclized with sodium methoxide by the method described in Section II (c). The product (1·5 g) formed very small colourless needles from methanol or glacial acetic acid of indefinite m.p. over 300 °C, giving a deep reddish brown ferric test in ethanol (Found : C, 55·5 ; H, 4·6%. Calc. for $C_{13}H_{13}O_5N$: C, 55·9 ; H, 4·7%). From its properties and analysis it is probably identical with the substance formulated as 4-hydroxy-2,6,7-trimethoxy-quinoline-3-carboxylic acid by Anet *et al.* (1952).

(h) *Methyl 2,4,6,7-Tetramethoxyquinoline-3-carboxylate (IIa).*—The substance IIb (0·2 g) was treated with diazomethane as described in Section II (a). The crude product was recrystallized from aqueous methanol yielding colourless needles (0·15 g), m.p. and mixed m.p. with the substance prepared in Section II (e) 117 °C (Found : C, 58·5 ; H, 5·4 ; CH_3O, 49·3%. Calc. for $C_{15}H_{17}O_6N$: C, 58·6 ; H, 5·6 ; $5 \times CH_3O$, 50·5%).

Treatment of the substance IIb (0·1 g) suspended in methanol (50 ml) with 1 equiv of ethereal diazomethane at 0° C gave unchanged starting material (0·04 g) and the same methylation product, m.p. 117 °C (0·03 g).

III. Acknowledgment

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GEIJERIN: A NEW COUMARIN FROM THE BARK OF *GEIJERA SALICIFOLIA* SCHOTT

By F. N. Lahey* and D. J. Wluka*

Summary

The bark of *Geijera salicifolia* Schott has yielded a new coumarin, geijerin, which has been shown to be 6-*iso*valeryl-7-methoxycoumarin.

I. Introduction

Geijera salicifolia Schott is a moderately sized tree widely distributed over the coastal area of central and southern Queensland. The bark of this species was collected for examination for alkaloids as part of a general programme involving the family Rutaceae. This species failed to yield any alkaloidal material but a new coumarin, geijerin, was isolated from it and the investigation of this substance forms the subject of this paper.

When a concentrated methanolic extract of the bark was allowed to stand in the refrigerator a brown solid precipitated from which geijerin, a white crystalline material was isolated by crystallization. Geijerin melts at 121 °C and from the results of elementary analyses and molecular weight determination (Signer), the composition $C_{15}H_{16}O_4$ has been assigned to it.

Geijerin contains one methoxyl group and one carbonyl group, the latter being shown by the preparation of a 2,4-dinitrophenylhydrazone, $C_{26}H_{20}O_7N_4$, m.p. 181 °C. Geijerin is insoluble in aqueous sodium carbonate but dissolves in aqueous sodium hydroxide (5%) on warming, giving a bright yellow solution from which the original material is precipitated by acid. Catalytic hydrogenation over palladium charcoal yielded dihydrogeijerin, $C_{15}H_{18}O_4$, m.p. 84 °C, which was not recovered by acidification of its alkaline solution, a phenolic acid, dihydrogeijerinic acid, $C_{15}H_{20}O_5$, m.p. 164 °C, being obtained instead. Methylation of geijerin with dimethyl sulphate and aqueous alkali produced methylgeijerinic acid, $C_{16}H_{24}O_5$, m.p. 158 °C, which on catalytic hydrogenation gave dihydromethylgeijerinic acid, $C_{16}H_{26}O_5$, m.p. 144 °C. These results are consistent with the presence of a coumarin nucleus.

Only five carbon atoms, one of which is present in a carbonyl group, remain to be identified. That these are present as an *iso*valeryl side-chain was shown by the alkali fusion of geijerin from which *iso*valeric acid was isolated and identified as its anilide, m.p. 110 °C. The second product of the reaction was resorcinol thus placing the methoxyl group in either the 5- or 7-position. Finally, the position of the *iso*valeryl side-chain was determined by alkaline permanganate

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oxidation of methylgeijerinic acid.   4,6-Dimethoxy*iso*phthalic acid was isolated and identified as its dimethyl ester, m.p. 150 °C (lit. 150 °C).

Geijerin, therefore, is 6-*iso*valeryl-7-methoxycoumarin (I).   Structurally, it is closely related to suberosin, which was shown by Ewing, Hughes, and Ritchie (1950) to be 6(γγ-dimethylallyl)-7-methoxycoumarin (II).   Dihydro-deoxygeijerin and tetrahydrosuberosin should, therefore, be identical.   No crystalline material could be isolated from the products of Clemmensen reduction of geijerin.   Hartung and Crossley (1934) had observed that some aromatic ketones are reduced to the corresponding alkylbenzenes by hydrogenation in
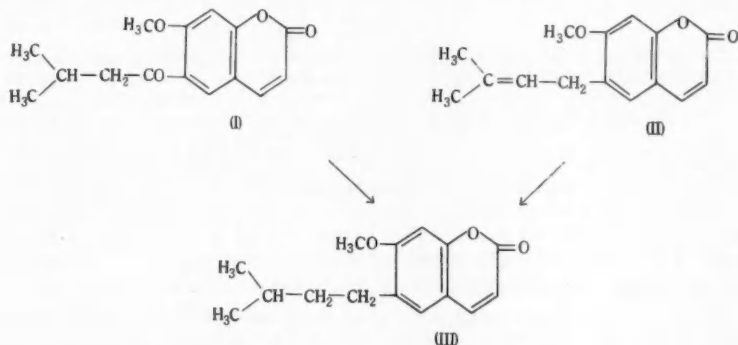
ethanol over palladized charcoal.   Under these conditions geijerin yielded only dihydrogeijerin.   When glacial acetic at 65 °C (Horning and Reisner 1949) was used as solvent for the hydrogenation, six atoms of hydrogen were taken up per molecule of geijerin.   The product obtained was a brown oil from which dihydro-deoxygeijerin (III), $C_{15}H_{20}O_3$, m.p. 49 °C, was isolated in poor yield.   No depression was observed on admixture with tetrahydrosuberosin, m.p. 48 °C, kindly supplied by Dr. G. K. Hughes.

II. EXPERIMENTAL

(a) *Isolation of Geijerin*.—The dried ground bark was exhausted with methanol in a Soxhlet apparatus, and the dark brown extract was concentrated to a thin syrup at atmospheric pressure. The concentrate on standing in a refrigerator deposited a brown solid which was filtered off and washed with some cold methanol.   The crude material was crystallized from methanol with charcoal ; at this stage the material had a light brown colour.   A dilute solution of this in pure dry benzene was filtered through a short column of alumina which absorbed the brown impurity. A final crystallization yielded pure geijerin, m.p. 121 °C, in flat colourless prisms.

Subsequently, it was found that the use of light petroleum to extract the bark greatly simplified the purification as only one recrystallization from methanol with charcoal was then necessary to obtain pure geijerin.   Yields of 0·6% of the dried bark were obtained (Found : C, 69·0 ; H, 6·2 ; CH_3O, 11·5% ; mol. wt. (Signer), 268. Calc. for $C_{15}H_{16}O_4$: C, 69·2 ; H, 6·2 ; CH_3O, 11·9%) (one methoxyl) ; mol. wt., 26.

(b) *2,4-Dinitrophenylhydrazone*.—The 2,4-dinitrophenylhydrazone was prepared by the usual procedure.   It crystallized from ethanol in orange-red hexagonal prisms, m.p. 181 °C Found : C, 57·3 ; H, 4·6 ; N, 12·9%.   Calc. for $C_{26}H_{20}O_7H_4$: C, 57·3 ; H, 4·6 ; N, 12·7%).

(c) *Dihydrogeijerin.*—*Geijerin* (1 g) was hydrogenated in the presence of palladized charcoal (10% ; 0·5 g) when a little more than the theoretical quantity of hydrogen was taken up. The product was recrystallized from a mixture of ethyl acetate and light petroleum giving colourless crystals, m.p. 84 °C (Found : C, 68·6 ; H, 6·8%. Calc. for $C_{15}H_{17}O_4$: C, 68·7 ; H, 6·9%).

(d) *Dihydrogeijerinic Acid.*—Dihydrogeijerin (0·1 g) was dissolved in aqueous alkali (5% ; 5 ml) and then dilute acid was added. The solid precipitate was recrystallized from aqueous ethanol giving colourless crystals, m.p. 164 °C (Found : C, 64·1 ; H, 7·2%. Calc. for $C_{15}H_{20}O_5$: C, 64·4 ; H, 7·1%).

(e) *Methylgeijerinic Acid.*—Geijerin (1 g) dissolved in methanol (15 ml) and aqueous alkali (20% ; 17 ml), was heated on a boiling water-bath, and was methylated with dimethyl sulphate at 60 °C. Worked up in the usual way, this yielded fine needles of methylgeijerinic acid from aqueous ethanol, m.p. 158 °C (yield 75%) (Found : C, 65·7 ; H, 6·9 ; CH_2O, 20·7%. Calc. for $C_{16}H_{20}O_5$: C, 65·6 ; H, 6·9 ; CH_3O, 21·2 (two methoxyls)).

(f) *Dihydromethylgeijerinic Acid.*—Methylgeijerinic acid (0·5 g) in ethanol was hydrogenated at room temperature and pressure in the presence of Adams's catalyst (5 mg), when slightly less than the theoretical amount of hydrogen for one double bond was absorbed. The product crystallized from ethanol in colourless needles, m.p. 144 °C, in almost quantitative yield (Found : C, 65·3 ; H, 7·3%. Calc. for $C_{16}H_{22}O_5$: C, 65·3 ; H, 7·4%).

(g) *Potash Fusion.*—Geijerin (3·0 g) was added in small quantities with stirring to fused potassium hydroxide at 250 °C. When addition was complete, heating was continued for 1 hr. The melt on cooling was dissolved in water, acidified, and extracted with ether. The residue remaining on removal of the ether was dissolved in aqueous alkali (5% ; 15 ml), which was then saturated with carbon dioxide and extracted with ether.

The ether extract yielded a brown oily solid which was drained overnight on a porous plate. A portion of the remaining solid was sublimed in vacuum, the sublimate being a white crystalline solid, m.p. 108 °C alone or admixed with an authentic sample of resorcinol. Fluorescein was formed in the phthalein reaction.

The bicarbonate solution, after having been extracted with ether was acidified with sulphuric acid and steam distilled. The distillate had the characteristic odour of a lower fatty acid. The fatty acid (0·2 g) obtained by extraction with ether was converted into its anilide via the acid chloride. Recrystallization from light petroleum (40–60 °C) gave colourless flaky crystals of the anilide of *iso*valeric acid, m.p. 110 °C (lit. 109–110 °C). No depression of m.p. was produced on admixture with an authentic sample (Found : N, 7·9%. Calc. for $C_{11}H_{15}OH$: N, 7·9%).

(h) *Oxidation of Methylgeijerinic Acid.*—Methylgeijerinic acid (0·5 g) was dissolved in aqueous alkali (1% ; 200 ml) and dilute potassium permanganate (1% ; 240 ml) was added until oxidation was complete. The manganese dioxide was filtered off and washed with hot water. After a few ml of ethanol had been added to the combined filtrate and washings to destroy any excess permanganate the solution was concentrated under reduced pressure to about 10–15 ml and acidified. On cooling, a white crystalline deposit was obtained, which on recrystallization had m.p. 260–266 °C with decomposition. The recorded m.p. of 4,6-dimethoxy*iso*phthalic acid is 264 °C with decomposition. The acid was methylated with diazomethane, and the double ester was recrystallized from ether in colourless platelets, m.p. 150 °C (lit. 150 °C for dimethyl ester) (Found : C, 56·5 ; H, 5·5%. Calc. for $C_{12}H_{14}O_6$: C, 56·7 ; H, 5·5%).

(i) *Dihydrodeoxygeijerin.*—Geijerin (0·5 g) was hydrogenated in glacial acetic acid at 65 °C over palladized charcoal (10% ; 1 g). The first molar equivalent of hydrogen was taken up rapidly, but the uptake of the remainder was considerably slower. Slightly more than the theoretical volume of hydrogen (3 molar equivalents) was consumed. The solvent was removed under reduced pressure leaving a brown oil which could not be crystallized. A portion of this oil was distilled in vacuum. The semicrystalline distillate was drained on a porous tile and the residue recrystallized from aqueous ethanol yielding colourless crystals of dihydrodeoxygeijerin, m.p. 49 °C. No depression was produced on admixture with an authentic sample of tetrahydrosuberosin.

III. Acknowledgments

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THE ALKALOIDS OF *KOPSIA LONGIFLORA* MERRILL

I. ISOLATION OF THE ALKALOIDS

By W. D. Crow* and M. Michael*

Summary

The bark and leaves of the rain-forest tree *Kopsia longiflora* Merrill (Apocynaceae) contain four new alkaloids; kopsinine, $C_{21}H_{26}O_2N_2$ (0·2 per cent.),* kopsilongine, $C_{24}H_{30}O_6N_2$ (0·06 per cent.), and kopsamine, $C_{25}H_{30}O_7N_2$ (0·02 per cent.) occurring in the bark; and kopsilongine (0·07 per cent.), kopsamine (0·3 per cent.), and kopsiflorine, $C_{23}H_{26}O_5N_2$ (0·04 per cent.) in the leaves. The bark also contains β-amyrin (0·35 per cent.) while the leaves afford a mixture of paraffin hydrocarbons, mainly *n*-hentriacontane, β-sitosterol, a sterol, $C_{29}H_{50}O_2$, and a triterpene alcohol acetate, $C_{32}H_{52}O_2$.

Kopsamine, kopsilongine, and kopsiflorine each contain two methoxyl groups, while kopsinine contains only one; kopsamine and kopsilongine also contain methylenedioxy-groups. No reactive carbonyl groups were detected. The alkaloids all titrated as monoacid bases and formed monomethiodides, while the ultraviolet spectra recorded in acid and neutral media show that the basic (tertiary) nitrogen atom does not contribute to the chromophoric system.

I. INTRODUCTION

The material for this investigation was collected in May 1953 near Mission Beach in northern Queensland, and the species was apparently confined tô that area. Preliminary tests (Webb 1952) had indicated the presence of alkaloids. The species, originally thought to be new, has been identified as *Kopsia longiflora* Merrill, which occurs in Luzon, Leyte, and Romblon Islands of the Philippine group. The genus *Kopsia* is placed by Engler and Prantl (1931) in the tribe Plumeriae of Apocynaceae together with the known alkaloid-containing genera (Henry 1949) *Alstonia*, *Vinca*, and *Tabernaemontana*, and several species have been cursorily examined by Greshoff (1890), who reported the occurrence of alkaloids in *K. albiflora* Boerl., *K. arborea* Blume, *K. roxburghii* Tharm. ex Wehmer., and *K. flavida* Blume, those of the last being crystalline. However, no physical constants were reported, and as the samples were no longer available, specimens of *K. flavida* were obtained from the Botanic Gardens of Indonesia at Bogor and examined for alkaloids. Kopsinine was isolated from the fruit, but no other similarity was confirmed. More recently Bhattacharya, Chatterjee, and Bose (1949) have described the isolation from *K. fruticosa* A.DC. of a new alkaloid kopsine, $C_{22}H_{26}O_4N_2$, and later degradative work (Bhattacharya 1953) has resulted in the identification of 2-methylindole and indole-2-carboxylic acid among the products of alkaline fusion, thus placing kopsine in the indole group of alkaloids.

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II. Separation and Properties of the Alkaloids

The crude alkaloids of the bark were separated by distribution of the hydrochlorides between chloroform and dilute hydrochloric acid (cf. isolation of novacine, Martin *et al.* 1952), that of kopsinine, $C_{21}H_{26}O_2N_2$, being insoluble in chloroform. The alkaloids with chloroform-soluble hydrochlorides could not be separated by crystallization or by chromatography, but fractional crystallization of the picrates afforded kopsamine, $C_{25}H_{30}O_7N_2$, as the minor constituent of the mixture and kopsilongine, $C_{24}H_{30}O_6N_2$, as the major constituent. The alkaloids of the leaves on the other hand contained no kopsinine, all the bases having chloroform-soluble hydrochlorides. Crystallization afforded kopsamine, a mixture of that base with kopsilongine, which was separated into its components as described above, and kopsiflorine, $C_{23}H_{28}O_5N_2$. The last was separated from the final mother liquors by means of its higher solubility in petroleum. The alkaloids are listed with their physical constants in Table 1.

Table 1
THE PHYSICAL CONSTANTS OF THE ALKALOIDS

Name	Formula	Melting Point (°C corr.)	$[\alpha]_D^{23}$	pK_a	Number of Methoxyl Groups	Labat $=O_2CH_2$ Test
Kopsinine ..	$C_{21}H_{26}O_2N_2$ ..	104–105	−76·9°	7·50	1	−ve
Kopsiflorine ..	$C_{23}H_{28}O_5N_2$ ..	144–145	−66·9°	6·38	2	−ve
Kopsilongine ..	$C_{24}H_{30}O_6N_2$ ..	206–208	−18·2°	6·80	2	+ve
Kopsamine ..	$C_{25}H_{30}O_7N_2$ ..	203–204	−46·4°	6·58	2	+ve

The alkaloids were all stable to mineral acids, were insoluble in sodium hydroxide solution, and gave no reaction with Brady's reagent. Electrometric titration showed them to be monobasic, and of similar basic strength except kopsinine, the strongest of the group. Each formed a crystalline monomethiodide, showing (in the absence of alkylimino-groups*) that the basic nitrogen atom is common to two rings. The alkaloids formed crystalline monoacid salts ; the one exception noted was kopsinine which formed a dihydrochloride, although it formed only the normal monopicrate. This apparent anomaly however may have been due to the method of preparation of the salt (cf. lupanine).

The ultraviolet absorption spectra of the alkaloids in neutral and acid solution are shown in Figure 1. It is evident from the similarity of the acid and neutral curves for each alkaloid that the basic nitrogen atom is not part of the chromophoric system. The spectra are generally similar in form, but fall

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* Kopsilongine and its derivatives repeatedly gave values for $2\cdot2$–$2\cdot5$ methoxyl groups in the Zeisel estimation, and the base itself analysed for $0\cdot3$ methylimino-groups. It was evident that the compound behaves anomalously in the Zeisel estimation, and decision concerning the presence of a methylimino-group must await further investigation. The other alkaloids behaved normally and contained no methylimino-groups.

into two groups.   Kopsamine and kopsilongine show a bathochromic shift of some 15 mμ in the 200–50 mμ region as compared to kopsinine and kopsiflorine. Assuming the presence of an aromatic nucleus, this shift may be ascribed to the presence in the former pair of ether (methylenedioxy-) linkages.   The somewhat higher intensity of absorption is in accord with this explanation.

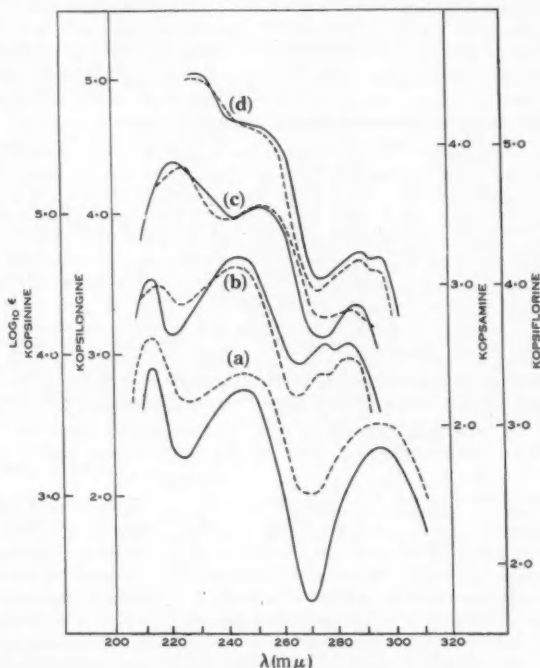The infra-red spectra have been recorded and will be reported in a subsequent paper.

Fig. 1.—The ultraviolet absorption spectra of the alkaloids.
(a) Kopsinine. (b) Kopsiflorine. (c) Kopsilongine. (d) Kopsamine.
——— In ethanol.
- - - - In N/10 ethanolic hydrochloric acid.

III. NON-BASIC CONSTITUENTS

The petroleum-soluble fraction of the bark extract, after removal of chlorophyll, contained only β-amyrin, and it is of interest to note that the same results were obtained with the bark of *K. flavida*.   The corresponding fraction from the leaves, however, was a complex mixture and was separated by repeated chromatography.

A hydrocarbon fraction, m.p. 66·5 °C, was isolated, and X-ray diffraction showed the long-chain spacing to be 41·4 Å for a pressed specimen and 41·2 Å for a melted specimen ; a synthetic sample of *n*-triacontane gave a spacing of

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40·1 Å in agreement with recorded values, while Robertson (1953) records 41·7 and 41·3 Å for n-hentriacontane. Piper *et al.* (1931) have shown that mixtures of hydrocarbons differing by less than four carbon atoms show only one modified spacing, so it may be concluded that the *Kopsia* hydrocarbon is a mixture consisting very largely of n-hentriacontane. The other constituents isolated were an unidentified sterol, $C_{29}H_{50}O_2$, an unidentified triterpene alcohol acetate, $C_{32}H_{52}O_2$, and β-sitosterol, identified by preparation of derivatives and comparison with authentic specimens.

IV. EXPERIMENTAL

All melting points are corrected unless otherwise stated. Microanalyses were carried out by the Australian Microanalytical Service under the direction of Dr. K. W. Zimmerman. The ultraviolet absorption spectra were measured on a Hilger Uvispek.

(a) *Extraction of the Leaves.*—The dried milled leaves (5·45 kg) were extracted with methanol in a Soxhlet apparatus and the concentrated extract freed from waxes and chlorophyll by extraction at 60 °C with petroleum (b.p. 100–110 °C). The petroleum ext act was washed with 2% hydrochloric acid to remove basic material and the methanol concentrate evaporated under reduced pressure, rendered ammoniacal, and exhaustively extracted with chloroform. The aqueous layer gave no tests for alkaloids or N-oxides and was discarded. The chloroform extracts were washed with 2% sodium hydroxide solution and water and evaporated to dryness. The residue was dissolved in benzene and the solution extracted with 5% hydrochloric acid until no further alkaloid was removed. All acid extracts were then combined, basified, and the alkaloids recovered into chloroform. Evaporation afforded a crude alkaloidal gum (38 g, 0·7%).

(i) *Examination of the Petroleum Extract.* The petroleum extract was dried and chromatographed on alumina (100 by 7 cm; activity I), the following fractions being collected :

A.	Petroleum (b.p. 40–60 °C)	2·5 g colourless wax
B.	Petroleum/ether 1 : 1	11·4 g yellow-green wax
C.	Ether	22·5 g green wax

Fraction *A*, after sublimation at 160 °C/0·05 mm and subsequent recrystallization from ethyl acetate afforded a hydrocarbon as glistening scales, m.p. 66·4–66·8 °C (Found : C, 85·4 ; H, 14·9%. Calc. for $C_{30}H_{62}$: C, 85·2 ; H, 14·8%, transition point on cooling 65·0 °C. The corresponding values reported by Piper *et al.* (1931) are for n-triacontane 65·6–65·8 °C and 64·3 °C, and for n-hentriacontane 67·6–67·8 °C and 66·2 °C. The long-chain spacings measured by X-ray diffraction were 41·4 Å for a pressed specimen and 41·2 Å for a melted specimen (both *A* spacings) ; Robertson (1953) records values of 41·7 and 41·3 Å for pressed and melted n-hentriacontane. A synthetic sample of n-triacontane gave a spacing of 40·4 Å.

Fraction *B* was rechromatographed in ether and crystallized from chloroform/methanol to give a *triterpene alcohol acetate* as colourless plates, m.p. 279–281 °C (Found : C, 82·1 ; H, 11·0 ; O, 7·0%. Calc. for $C_{32}H_{52}O_2$: C, 82·0 ; H, 11·2 ; O, 6·8%). The acetate had $[\alpha]_D^{23} \pm 0°$ (*c*, 1·2 in chloroform), gave a yellow Liebermann/Burchardt test, and was hydrolysed by methanolic potassium hydroxide to the parent *alcohol* which crystallized from methanol as colourless needles, m.p. 203–204 °C (Found : C, 84·5 ; H, 11·6 ; O, 3·9%. Calc. for $C_{30}H_{50}O$: C, 84·5 ; H, 11·8 ; O, 3·8%). The alcohol had $[\alpha]_D^{23} -20·8°$ (*c*, 0·34 in chloroform), gave a red-brown Liebermann/Burchardt test and was reconverted to the acetate on acetylation.

Fraction *C* was rechromatographed in petroleum (40–60 °C), which eluted 4·8 g high-boiling oils. Ether eluted 3·0 g material which after sublimation at 186 °C/0·1 mm afforded 0·3 g *sterol* as colourless needles, 215–217 °C (Found : C, 80·8 ; H, 11·9 ; O, 7·7%. Calc. for $C_{29}H_{50}O_2$: C, 80·9 ; H, 11·7 ; O, 7·4%), giving a blood-red Liebermann/Burchardt test and affording with acetic anhydride/pyridine an acetate, m.p. 261–263 °C. Further elution with chloroform afforded β-sitosterol, colourless needles, m.p. 139–140 °C (Found : C, 82·5 ; H, 12·0 ; O, 5·5%. Calc. for $C_{29}H_{50}O.\frac{1}{2}H_2O$: C, 82·2 ; H, 12·1 ; O, 5·6%). It had $[\alpha]_D^{23} -38·8°$ (*c*, 0·38 in chloroform)

and gave an acetate, m.p. 130–131 °C (Found : C, 81·5 ; H, 11·4 ; O, 7·4%.   Calc. for $C_{31}H_{52}O_2$:
C, 81·5 ; H, 11·5 ; O, 7·0%).   Values reported in the literature range from 135 to 137 °C for
β-sitosterol and 120 to 127 °C for its acetate.   King and Jurd (1953) quote m.p. 136·5 °C,
$[\alpha]_D^{25}$ —33° for the alcohol, and m.p. 120 °C for the acetate.

(ii) *Examination of the Crude Bases.*   The crude alkaloidal gum was shaken out of benzene
with 0·5% hydrochloric acid ; subsequent use of stronger acid removed only dark intractable
material.   The recovered bases were crystallized from methanol, affording a first crop of crude
kopsamine (10·4 g) as prisms, m.p. 195–197 °C, and a second crop of colourless needles (5·26 g),
m.p. 172–178 °C, which was a mixture.   The mother liquors were evaporated and the residue
chromatographed over alumina in benzene, which eluted 7·86 g ;   chloroform and methanol
subsequently eluted 5·96 g intractable gum, which was set aside.   The material eluted by benzene
crystallized from methanol to give 3·87 g mixed bases.   The petroleum-soluble portion of the
residual 3·99 g bases afforded 2·46 g *kopsiflorine.*

The mixed fractions obtained above were subjected to partition chromatography on buffered
kieselguhr, eluting with petroleum (40–60 °C).   No separation took place at pH 3·9, 5·2, and
6·0, but at pH 7·1, 8·0, and 8·9 twin peaks were observed.   The degree of separation was
insufficient for effective utilization, however, and the method was abandoned.   Chromatography
on alumina or silica gel was equally unsuccessful, a single peak being obtained in both cases,
while counter-current crystallization of the mixture achieved only a slight purification after 25
operations.   Separation was ultimately achieved by counter-current crystallization of the
picrates from methanol/acetone, kopsamine picrate being the less soluble in this system.   The
more soluble picrate consisted of long silky needles whereas the less soluble was usually obtained
as compact rosettes of thick leaflets.   This visual identification was found to be more convenient
and reliable than m.p. determination, particularly as neither picrate had a distinct m.p. but
coalesced to a gum before undergoing decomposition at temperatures varying with the conditions
of the measurement.   The number of operations required to achieve full separation varied with
the composition of the mixture, but 10–15 " plates " was usually sufficient.   Separation in this
way afforded *kopsilongine* (3·6 g, m.p. 206–208 °C) and kopsamine (5·5 g, m.p. 203–204 °C).
A mixture of the two alkaloids had m.p. 181–186 °C and this was not greatly altered by change in
composition of the mixture.

(*b*) *Extraction of the Bark.*—The milled bark (2·35 kg) was extracted with methanol and
the extract worked up as described for the leaves.

(i) *Examination of the Petroleum Extract.*   The washed, dried extract was chromatographed
over alumina, eluting first with petroleum (40–60 °C), and then with ether.   The combined
eluates were evaporated, yielding β-amyrin (8·25 g) as colourless needles, m.p. 204–205 °C
(Found: C, 84·5 ; H, 11·8%.   Calc. for $C_{30}H_{50}O$: C, 84·5 ; H, 11·8%) and $[\alpha]_D^{23}$ +91°
(c, 0·90 in chloroform).   The acetate, prepared by direct recrystallization from acetic anhydride,
was obtained as colourless needles, m.p. 242–243 °C (Found : C, 82·0 ; H, 11·1%.   Calc. for
$C_{32}H_{52}O_2$: C, 82·0 ; H, 11·2%) and $[\alpha]_D^{23}$ +82·8° (c, 0·8 in chloroform), while the benzoate
had m.p. 237–238 °C and $[\alpha]_D^{23}$ +86° (c, 0·81 in chloroform).   The identity was confirmed by
comparison with authentic specimens.   Musgrave and Wagner (1952) record rotations of 82·5
and 98·0° for the acetate and benzoate respectively.

(ii) *Examination of the Crude Bases.*   The crude base mixture (7·55 g) was submitted to a
5-plate counter-current distribution between 2% hydrochloric acid and chloroform.   Recovery
of the bases from the acid solutions in the usual manner afforded *kopsinine* (4·68 g) as prisms,
m.p. 101–103 °C from petroleum (40–60 °C).   The bases not extracted from chloroform were
recovered and chromatographed over alumina in benzene, which eluted 1·88 g material crystal-
lizing from methanol as colourless needles, m.p. 175–178 °C.   Further elution with chloroform
afforded 0·57 g intractable gum, which was set aside.   The crystalline material was separated
via the picrates into kopsamine (0·42 g) and kopsilongine (1·32 g).

(*c*) *Properties of the Alkaloids.*—(i) *Kopsamine.*   This alkaloid separated from methanol
or acetone as colourless prisms, m.p. 203–204 °C (Found : C, 63·7 ; H, 6·4 ; N, 6·2 ; CH_3O,
13·5 ; CH_3N, nil ; CH_3C, nil ; act. H, 0·40%.   Calc. for $C_{25}H_{26}O_7N_2$: C, 63·8 ; H, 6·4 ;

N, $6\cdot0$; $2\times CH_3O$, $13\cdot2$; $2\times$act. H, $0\cdot44\%$) and $[\alpha]_D^{23}$ $-46\cdot4°$ (c, $1\cdot01$ in chloroform). The alkaloid gave a positive methylenedioxy test, a green colour with concentrated nitric acid, and a cherry-red colour with potassium dichromate/concentrated sulphuric acid (Otto test). It was unaffected by treatment with Brady's reagent, diazomethane, cold 20% hydrochloric acid, nitrous acid, or acetic anhydride/pyridine at 100 °C, and was insoluble in 2% sodium hydroxide solution. Electrometric titration at 20 °C in 70% methanol showed it to be monobasic, pK_a $6\cdot58$. The *perchlorate* crystallized from water as colourless needles, m.p. 242–243 °C (decomp.) (Found: C, $52\cdot3$; H, $5\cdot5$; N, $4\cdot6$; Cl, $6\cdot7\%$. Calc. for $C_{25}H_{30}O_7N_2.HClO_4$: C, $52\cdot5$; H, $5\cdot5$; N, $4\cdot9$; Cl, $6\cdot2\%$). The nitrate, oxalate, and tartrate also crystallized readily from water, but had inconsistent m.p.'s. The *methiodide* was obtained from ethanol as colourless needles, m.p. 236 °C (decomp.) (Found: C, $49\cdot3$; H, $5\cdot6$; N, $4\cdot6$; I, $20\cdot2$; CH_3O, $9\cdot9\%$. Calc. for $C_{25}H_{30}O_7N_2.CH_3I.H_2O$: C, $49\cdot5$; H, $5\cdot6$; N, $4\cdot4$; I, $20\cdot2$; $2\times CH_3O$, $9\cdot8\%$).

(ii) *Kopsilongine*. The alkaloid crystallized from methanol, or acetone, as colourless plates, or needles, m.p. 206–208 °C (Found: C, $65\cdot0$, $65\cdot1$; H, $7\cdot0$, $6\cdot8$; O, $22\cdot2$; N, $6\cdot4$; CH_3O, $18\cdot0$, $18\cdot5$, $18\cdot1$; CH_3N, $1\cdot2$, $0\cdot4$; CH_3C, nil; act. H, $0\cdot5\%$; mol. wt. (Rast), 457. Calc. for $C_{24}H_{30}O_6N_2$: C, $65\cdot1$; H, $6\cdot8$; O, $21\cdot7$; N, $6\cdot3$; $2\times CH_3O$, $14\cdot0$; $2\times$act. H, $0\cdot5\%$; mol. wt., 443) and had $[\alpha]_D^{23}$ $-18\cdot2°$ (c, $0\cdot99$ in chloroform). The alkaloid gave a positive methylenedioxy test and was indistinguishable from kopsamine in its colour reactions and behaviour to the reagents listed. Electrometric titration in 70% methanol indicated that it was a monoacid base, pK_a $6\cdot80$. The *perchlorate* crystallized from water as colourless plates darkening from 230 °C and decomposing at 246–248 °C (Found: C, $52\cdot9$; H, $5\cdot6$; N, $5\cdot1$; Cl, $6\cdot9$; CH_3O, $13\cdot9\%$. Calc. for $C_{24}H_{30}O_6N_2.HClO_4$: C, $53\cdot1$; H, $5\cdot8$; N, $5\cdot2$; Cl, $6\cdot5$; $2\times CH_3O$, $11\cdot4\%$). The *methiodide* was obtained from methanol/acetone as colourless needles which puffed up at 184 °C and decomposed at 228–230 °C (Found: C, $49\cdot6$; H, $6\cdot2$; O, $18\cdot9$; N, $4\cdot6\%$. Calc. for $C_{24}H_{30}O_6N_2.CH_3I.H_2O$: C, $49\cdot8$; H, $5\cdot9$; O, $18\cdot6$; N, $4\cdot7\%$). A sample dried at 65 °C/$0\cdot01$ mm over phosphorus pentoxide showed the same m.p. behaviour (Found: C, $51\cdot3$; H, $5\cdot9$; CH_3O, $11\cdot9\%$. Calc. for $C_{24}H_{30}O_6N_2.CH_3I$: C, $51\cdot3$; H, $5\cdot7$; $2\times CH_3O$, $10\cdot6\%$).

(iii) *Kopsiflorine*. The substance was obtained from petroleum as colourless needles, m.p. 144–145 °C (Found: C, $67\cdot2$; H, $6\cdot9$; O, $19\cdot6$; N, $7\cdot1$; CH_3O, $14\cdot6$; CH_3N, nil; CH_3C, nil; act. H, $0\cdot5\%$. Calc. for $C_{23}H_{28}O_5N_2$: C, $66\cdot9$; H, $6\cdot9$; O, $19\cdot4$; N, $6\cdot8$; $2\times CH_3O$, $14\cdot8$; $2\times$act. H, $0\cdot5\%$) and had $[\alpha]_D^{23}$ $-66\cdot9°$ (c, $1\cdot41$ in chloroform). It gave no methylenedioxy test, a pale yellow colour with concentrated nitric acid, and a cherry-red colour with concentrated sulphuric acid/potassium dichromate. Kopsiflorine did not react with Brady's reagent, was insoluble in 2% sodium hydroxide solution, and was recovered unchanged after treatment with nitrous acid or cold 20% hydrochloric acid. Electrometric titration at 20 °C in 70% methanol showed kopsiflorine to be a monoacid base of pK_a $6\cdot38$. The *methiodide* crystallized from ethanol in colourless needles, m.p. 211–213 °C (Found: C, $51\cdot1$; H, $5\cdot7$; N, $4\cdot7$; I, $22\cdot4\%$. Calc. for $C_{23}H_{28}O_5N_2.CH_3I.\frac{1}{2}H_2O$: C, $51\cdot2$; H, $5\cdot7$; N, $5\cdot0$; I, $22\cdot5\%$).

(iv) *Kopsinine*. The alkaloid crystallized from petroleum (40–60 °C) as colourless prisms, m.p. 104–105 °C (Found: C, $74\cdot6$; H, $7\cdot6$; O, $9\cdot3$; N, $8\cdot2$; CH_3O, $9\cdot4$; CH_3N, nil; CH_3C, nil; act. H, $0\cdot6\%$. Calc. for $C_{21}H_{26}O_2N_2$: C, $74\cdot5$; H, $7\cdot7$; O, $9\cdot5$; N, $8\cdot3$; CH_3O, $9\cdot2$; $2\times$act. H, $0\cdot6\%$) and had $[\alpha]_D^{23}$ $-76\cdot9°$ (c, $2\cdot09$ in chloroform). Electrometric titration in 70% methanol showed the alkaloid to be monobasic, pK_a $7\cdot50$. The alkaloid gave no methylenedioxy test, no colour with concentrated nitric acid, nor with potassium dichromate/concentrated sulphuric acid, and failed to react with Brady's reagent. It was recovered unchanged after treatment with nitrous acid, diazomethane, or cold 20% hydrochloric acid, and was insoluble in 2% sodium hydroxide solution. The *dihydrochloride* crystallized from ethanol in colourless needles, m.p. 253–254 °C (Found: C, $61\cdot3$; H, $6\cdot8$; N, $6\cdot6$; Cl, $17\cdot4$; CH_3O, $7\cdot4\%$. Calc. for $C_{21}H_{26}O_2N_2.2HCl$: C, $61\cdot3$; H, $6\cdot9$; N, $6\cdot8$; Cl, $17\cdot3$; CH_3O, $7\cdot5\%$). The *picrate* was obtained from ethanol as yellow needles, m.p. 222–223 °C (Found: C, $57\cdot5$; H, $5\cdot0$; N, $12\cdot4\%$. Calc. for $C_{21}H_{26}O_2N_2.C_6H_3O_7N_3$: C, $57\cdot1$; H, $5\cdot2$; N, $12\cdot3\%$), while the *methiodide* crystallized from ethanol as colourless needles, m.p. 265–266 °C (Found: C, $55\cdot0$; H, $6\cdot1$; N, $5\cdot8$; I, $26\cdot3\%$. Calc. for $C_{21}H_{26}O_2N_2.CH_3I$: C, $55\cdot0$; H, $6\cdot1$; N, $5\cdot8$; I, $26\cdot4\%$).

(d) *Examination of* K. flavida.—Bark, fruit, and leaves (each 100 g) were separately extracted as described above and the crude bases isolated in the usual manner. The R_F values for the extracts are recorded below ; the solvent system used consisted of an 80 : 17 : 3 mixture by volume of n-butanol/water/acetic acid, and the papers were irrigated by ascending flow and developed with iodine vapour :

Bark extract	0·57, 0·63,	Kopsilongine	0·71
	0·74, 0·87	Kopsamine	0·72
Leaf extract	0·45, 0·74	Kopsinine	0·67
Fruit extract	0·59, 0·65	Kopsiflorine	0·75

Application of the kopsinine isolation procedure to the fruit extract afforded a small quantity of this base (m.p. and mixed m.p.) ; the other extracts gave no identifiable material. β-Amyrin was readily isolated from the bark, and was identified by comparison with an authentic sample from *K. longiflora*.

V. Acknowledgments

The authors are indebted to Mr. L. J. Webb, Division of Plant Industry, C.S.I.R.O., for the preliminary testing and arrangement of the supplies of material, to Mr. L. Smith of the Queensland National Herbarium, and Dr. L. M. Perry of the Arnold Arboretum, Jamaica Plains, Mass., U.S.A., for the identification of the species, and to Mr. P. Hunter, Division of Industrial Chemistry, C.S.I.R.O., for the extraction of the plant material. The specimens of *K. flavida* were supplied by Mr. J. Douglas, Curator of the Botanic Gardens of Indonesia at Bogor, whose generous cooperation is gratefully acknowledged. The authors also wish to thank Mr. J. Fridrichson, Division of Industrial Chemistry, C.S.I.R.O., for the X-ray measurements on the hydrocarbon, and Dr. R. J. Meakins, Division of Electrotechnology, C.S.I.R.O., for a sample of pure n-triacontane.

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THE ALKALOIDS OF *LUPINUS VARIUS* L.*

I. ISOLATION OF THE ALKALOIDS

By W. D. Crow† and N. V. Riggs†‡

Summary

The seeds of *Lupinus varius* L. (Leguminosae), used in parts of Western Australia as sheep fodder, contain an alkaloid LV–1, $C_{15}H_{23}ON_3$ (0·20 per cent.), (+)-*epi*lupinine (0·13 per cent.), (+)-*epi*lupinine-N-oxide (0·94 per cent.), and traces of an alkaloid LV–2. The N-oxide represents the first reported natural occurrence of such a compound in the lupinine group.

I. INTRODUCTION

Although lupins are known to be generally toxic and have formed the subject of numerous alkaloid researches (Henry 1949 ; Manske and Holmes 1953), selected strains of low alkaloid content (" sweet lupins ") have been used as fodder for many years. *Lupinus varius* L., a naturalized European species, has been extensively and successfully used for this purpose in parts of Western Australia, particularly in the Gingin, Dandarragan, and Geraldton districts. The seeds and dried plant only are consumed, sheep refusing to eat the aerial portions of the plant except in the early stages soon after germination (Norris 1943). The species has flourished in these districts with the result that on many properties almost the whole area is under lupins. During the 1949–51 seasons heavy sheep mortalities were experienced in the lupin areas and it was decided to examine the seeds for alkaloids. White (1951) had examined plants grown in New Zealand from Australian seed and isolated a crude alkaloidal gum in 0·45 per cent. yield from the seed. Distillation afforded a little (+)-*epi*lupinine (1-hydroxymethylquinolizidine), but the bulk of the material proved to be intractable and the examination was not pursued further.

II. ISOLATION OF THE ALKALOIDS

Examination of a crude methanolic extract of the seeds by paper chromatography showed the presence of at least four alkaloids with R_F values of 0·51, 0·37, 0·23, and 0·10. The known (+)-*epi*lupinine had R_F 0·37. The compound of R_F 0·51 could not be extracted from an alkaline solution during the working-up process, and as its R_F was identical with that of authentic (+)-*epi*lupinine-N-oxide the extracted alkaline liquors were reduced with zinc dust and acid. Subsequent

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treatment resulted in the isolation of large amounts of $(+)$-*epi*lupinine and in a later extraction the natural N-oxide was isolated directly by extraction with n-butanol. It is worth noting that this compound although present in $0 \cdot 94$ per cent. yield would escape the normal isolation processes used for alkaloids. N-oxides of the lupanine (C_{15}) group have been recorded before, but this is the first report of an N-oxide in the lupinine (C_{10}) group. No trace of any other N-oxide was detected.

The extractable bases consisted of a viscous gum and no separation could be achieved by the usual methods of solvent treatment or by the use of sparingly soluble salts. Partition chromatography on buffered kieselguhr at various pH values ranging from $4 \cdot 0$ to $9 \cdot 0$ was unsuccessful, the bases being eluted in mixed peaks in all cases, but chromatography over alumina showed some separation. The best results were obtained with activity I alumina using chloroform as the eluting solvent. A new base of R_F $0 \cdot 23$ designated as LV–1 was eluted almost on the solvent front and was closely followed by $(+)$-*epi*lupinine as a broad band consistent with its alcoholic nature. On adding a little ethanol to the eluting solvent the long " tail " of the $(+)$-*epi*-lupinine band was eluted together with another base of R_F $0 \cdot 10$ (Base LV–2) and a little $(+)$-*epi*lupinine-N-oxide. The presence of this last constituent possibly serves to explain the failure of White to obtain any substantial separation by distillation methods, as this compound decomposed on heating to give a variety of products. In subsequent extractions it was removed by washing the crude bases with water before chromatographing. Due to the rapid elution of the two major bases it was necessary to rechromatograph some mixed fractions in order to achieve full separation. Base LV–1 was obtained crystalline with some difficulty and had m.p. 108 °C and $[\alpha]_D^{23}$ $-314°$, R_F $0 \cdot 23$. It analysed for $C_{15}H_{22}ON_2$ and gave a monoperchlorate and a monomethiodide. It does not agree in physical constants with any of the known Lupin-type bases and is presumed to be new ; structural investigations at present in progress will be reported in a subsequent paper. $(+)$-*epi*Lupinine had essentially the constants quoted by White and was identified by comparison of suitable derivatives with authentic specimens. The methiodide, m.p. 251–252 °C, reported for this base was isolated and shown to have $[\alpha]_D^{23}$ $+1 \cdot 7°$. It is proposed that this compound be known as the α-methiodide, since examination of the mother liquors from its preparation has resulted in the isolation of the second β-meth-iodide, m.p. 265 °C and $[\alpha]_D^{23}$ $+0 \cdot 9°$ to be expected on stereochemical grounds.

For the purification of Base LV–2 partition chromatography in n-butanol/acetic acid on cellulose powder was used. In this way it was possible to remove all other basic constituents and obtain the alkaloid as a dark brown gum from which a small amount of the crystalline hydrochloride was obtained. Owing to the small quantity available complete purification could not be achieved, but analytical results indicated a formula of the order of $C_{15}H_{24}O_2N_2.HCl$.

The alkaloids, except Base LV–2, are at present the subject of biological testing in the Division of Animal Health and Nutrition, C.S.I.R.O., and details of the results will be published elsewhere. Preliminary tests indicate that the new Base LV–1 is the most toxic of the group.

III. EXPERIMENTAL

All m.p.'s are corrected unless otherwise stated. Microanalyses were carried out by the Australian Microanalytical Service under the direction of Dr. K. W. Zimmermann. All R_F values were measured on Whatman No. 1 paper with a solvent consisting of n-butanol/water/acetic acid in the ratio 80 : 17 : 3 by volume. Light petroleum refers to the hydrocarbon fraction b.p. 50–70 °C.

(a) *Extraction of the Seeds.*—The milled seeds (11·11 kg) were exhausted with methanol in a glass Soxhlet (the use of a metal extractor gave low yields of N-oxide and correspondingly high yields of (+)-*epi*lupinine) and the solvent removed (no steam-volatile alkaloids were detected). Fats and waxes were then removed by stirring with petroleum (b.p. 100–110 °C) at 60 °C and the aqueous layer acidified with hydrochloric acid and shaken several times with methylene chloride. The acid solution was then basified to pH 12 and extracted several times with chloroform to remove the extractable bases which were obtained on evaporation as a deep red-brown gum (47 g, 0·42%) of R_F 0·51, 0·37, 0·23, and 0·10.

(i) (+)-epi*Lupinine-N-oxide.* The alkaline liquors from the extraction were divided into two equal portions *A* and *B*. The former was acidified with 10N hydrochloric acid to pH 1 and stirred with zinc dust for 2 hr, then basified to pH 13, filtered, and extracted several times with chloroform. Evaporation afforded (+)-*epi*lupinine (47·5 g corresponding to 0·94% yield of the N-oxide) crystallizing from light petroleum in colourless needles, m.p. 77–78 °C (Found : C, 71·3 ; H, 11·5 ; O, 9·3 ; N, 8·5%. Calc. for $C_{10}H_{19}ON$: C, 70·9 ; H, 11·4 ; O, 9·5 ; N, 8·3%), undepressed by admixture with an authentic sample. Examination of the mother liquors by paper chromatography showed only one spot at R_F 0·37 ((+)-*epi*lupinine). The portion *B* was extracted five times with n-butanol and the combined extracts evaporated to dryness under reduced pressure. The crystalline residue gave (+)-*epi*lupinine-N-oxide from methanol/acetone as colourless hygroscopic needles, m.p. 212–215 °C (decomp.) (Found : C, 64·8 ; H, 10·4 ; N, 7·4%. Calc. for $C_{10}H_{19}O_2N$: C, 64·9 ; H, 10·3 ; N, 7·6%) undepressed by admixture with an authentic sample prepared by the action of 30% hydrogen peroxide on (+)-*epi*lupinine. The natural product was quantitatively reduced to the parent base by zinc dust in acid solution. On heating to its m.p. or refluxing for 2 hr in methanolic acetic acid it decomposed to give at least 10 products as revealed by paper chromatography.

(ii) (+)-epi*Lupinine and Base LV–1.* The extractable bases were chromatographed over activity I alumina in dry chloroform on a column 100 by 5 cm, the flow-rate being controlled at *c.* 3 c.c. min⁻¹, and fractions of 100 c.c. were collected. Each fraction was examined by paper chromatography ; 1–3 contained only *Base LV-1,* 4–6 were mixtures of Base LV-1, and (+)-*epi*lupinine and 7–16 contained only (+)-*epi*lupinine. Subsequent fractions eluted by chloroform/1–5% methanol contained (+)-*epi*lupinine, Base LV-2, and the dark resinous materials usually retained at the top of the column. After retreatment of fractions 4–6 there was finally obtained 22·3 g (0·20%) Base LV-1, 13·9 g (0·13%) (+)-*epi*lupinine and a dark gum (2·8 g) containing Base LV-2. Base LV-1 crystallized from acetone/light petroleum in colourless needles, m.p. 108–109 °C (Found : C, 73·4 ; H, 9·0 ; N, 11·4%. Calc. for $C_{15}H_{22}ON_2$: C, 73·2 ; H, 9·0 ; N, 11·4%) and $[\alpha]_D^{23}$ −314° (*c,* 0·6 in methanol). The *perchlorate* crystallized with difficulty from 95% ethanol as cream needles, m.p. 160–162 °C (decomp.) (Found : C, 50·3 ; H, 6·6 ; O, 24·8%. Calc. for $C_{15}H_{22}ON_2.\frac{1}{2}H_2O$: C, 50·6 ; H, 6·8 ; O, 24·9%) and darkened on exposure in solution. The *methiodide* crystallized slowly from ethanol in cream nodules, m.p. 246–248 °C (decomp.) (Found : C, 49·1 ; H, 6·5 ; N, 6·9%. Calc. for $C_{15}H_{22}ON_2.CH_3I$: C, 49·3 ; H, 6·5 ; N, 7·2%). The alkaloid was readily soluble in all solvents, except petroleum, and gave a deep red colour with ferric chloride indicating the possible presence of an α-pyridone nucleus.

(+)-*epi*Lupinine was obtained from light petroleum as colourless needles, m.p. 77–78 °C and $[\alpha]_D^{23}$ +36·6° (*c,* 0·97 in methanol) and afforded a picrate, m.p. 147–148 °C and a methiodide, m.p. 251–252 °C. White (1951) records m.p. 75–76 °C and $[\alpha]_D^{23}$ +35° for the alkaloid and m.p. 144 °C and 247–248 °C for the picrate and methiodide respectively. The dipicrate, m.p. 91–93 °C recorded by this author could not be prepared, but the identity was established by

comparison of the above derivatives with authentic specimens. Large-scale preparation of the methiodide resulted in the isolation from the mother liquors of the diastereoisomeric β-*methiodide*, m.p. 265 °C and $[\alpha]_D^{23}$ $+0\cdot9\pm0\cdot1°$ (c, $1\cdot98$ in methanol) (Found : C, $42\cdot6$; H, $7\cdot2$; O, $5\cdot3$; N, $4\cdot1$; I, $40\cdot9\%$. Calc. for $C_{10}H_{19}ON.CH_3I$: C, $42\cdot5$; H, $7\cdot1$; O, $5\cdot1$; N, $4\cdot5$; I, $40\cdot8\%$) as well as the known methiodide, m.p. 251–252 °C and $[\alpha]_D^{23}$ $+1\cdot7\pm0\cdot1°$ (c, $2\cdot36$ in methanol). (+)-*epi*Lupinine had pK_a $9\cdot0$ at 25 °C in 70% methanol.

(iii) *Base LV–2.* Cellulose powder (Whatman ; 250 g) was suspended in n-butanol previously saturated with 5% acetic acid and the butanol-saturated acetic acid (125 c.c.) added with shaking to ensure even distribution. The excess solvent was decanted and the thick slurry packed tightly into a column with a ramrod and perforated plunger. When packed the column had a bed-volume of 400 c.c. and a total volume of 500 c.c. After checking the solvent front with a solution of methyl orange the crude LV–2 fraction was applied in n-butanol (50 c.c.) and elution commenced with the previously equilibrated solvent. Fractions of 200 c.c. were collected, evaporated to small volume, and examined by paper chromatography. After the passage of $2\cdot5$ l. solvent Base LV–2 was eluted as a group of eight fractions and was recovered in the usual way. The resultant brown gum was dissolved in a little methanol, 10N hydrochloric acid added, and the mixture cautiously diluted with acetone. After several weeks the *hydrochloride* crystallized in low yield and was purified by recrystallization as described above. It formed cream nodules, m.p. 238–240 °C (Found : C, $58\cdot9$; H, $8\cdot0$; O, $10\cdot3$; N, $8\cdot7\%$) and had R_F $0\cdot10$. There was insufficient material for further investigation.

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SHORT COMMUNICATIONS

THE DIPOLE MOMENTS OF BROMOBENZENE, METHYL IODIDE, AND IODOBENZENE AS VAPOURS*

By R. J. W. Le Fèvre† and D. A. A. S. Narayana Rao†

An equation devised empirically by Buckingham and Le Fèvre (1952), to convert apparent dipole moments determined for solutes in benzene into the true values obtainable from measurements on the same solutes as gases, was recently tested by Le Fèvre and Le Fèvre (1954) on 15 compounds dissolved in carbon tetrachloride.

With the three substances of the above title the literature allowed doubt concerning the correct μ_{gas} (obs.) with which to check μ_{gas} (calc.). Debye relationships,

$$P = A + \frac{B}{T}$$

connecting total polarizations and absolute temperatures, were available for the first two vapours only, and the moments deduced therefrom varied, with bromobenzene from $1\cdot71$ to $1\cdot77$ D and with methyl iodide from $1\cdot3$ to $1\cdot6$ D. The moment of iodobenzene as a gas had been once recorded (Hurdis and Smyth 1942) but the value quoted, $1\cdot70$ D, was deduced by the refractivity method, and was higher than the μ_{gas} (calc.) expected by Le Fèvre and Le Fèvre. (When compiling their Table 3 the last-named authors overlooked the reference to the paper by Hurdis and Smyth, it is omitted also in the M.I.T. Tables of Wesson 1948.) Redeterminations have therefore been made on these materials.

Experimental

Pure dry specimens were redistilled immediately prior to introduction into apparatus of the type described by Le Fèvre (1953, Ch. 2), by which polarizations were measured relatively to carbon dioxide or benzene by methods set out by this author. Results are tabulated (Table 1) under usual headings.

Discussion

The moments now obtained are: CH_3I, $1\cdot64$ D; C_6H_5Br, $1\cdot70$ D; C_6H_5I, $1\cdot71$ D, in each case $\pm 0\cdot03$ D. From Table 2 it will be seen that μ_{gas} (calc.) by the equation of Buckingham and Le Fèvre is for these three substances lower than the observed value. The discrepancy is greatest with iodobenzene and least with methyl iodide. The three compounds are instances where $n_1^2 - n_2^2$ is algebraically negative.

TABLE 1

TEMPERATURE DEPENDENCE OF POLARIZATIONS

Temp. (°A)	$P_{obs.}$ (c.c.)	$P_{calc.}$* (c.c.)	Temp. (°A)	$P_{obs.}$ (c.c)	$P_{calc.}$* (c.c.)	Temp. (°A)	$P_{obs.}$ (c.c.)	$P_{calc.}$* (c.c.)
Bromobenzene†			Methyl iodide†			Iodobenzene‡		
362	83·4	83·5	291	75·4	75·0	432	80·4	80·0
384	81·1	80·7	292	74·2	74·8	447	78·2	78·6
420	76·6	76·7	313	70·4	71·0	458	77·7	77·7
424	75·7	76·3	328	69·3	68·6	481	75·7	75·8
441	74·9	74·7	353	65·0	65·1	512	73·2	73·5
476	72·2	71·8	369·5	63·6	63·0	530	72·7	72·4
486	70·9	71·0	389	60·6	60·8	541·5	71·5	71·7
			411	58·4	58·5	564	70·5	70·4
			432	57·0	56·6			
			457	53·9	54·5			

* From the following Debye equations (fitted to $P_{obs.}$ by least squares) :

$$C_6H_5Br, \quad P = (34\cdot8 \pm 1\cdot5) + (17630 \pm 621)/T,$$
$$CH_3I, \quad P = (18\cdot6 \pm 1\cdot1) + (16420 \pm 399)/T,$$
$$C_6H_5I, \quad P = (38\cdot8 \pm 1\cdot2) + (17810 \pm 580)/T,$$

† CO_2, $P = 7\cdot341$ c.c., as calibrating vapour.

‡ C_6H_6, $P = 27\cdot0$ c.c., as calibrating vapour.

TABLE 2

COMPARISON OF μ_{gas} (CALC.) AND μ_{gas} (OBS.)

Compounds	μ_{CCl_4}	μ_{gas} Calculated by Formula (1)	μ_{gas} Calculated by Le Fèvre and Le Fèvre (1954)	μ_{gas} (obs.)
CH_3Cl	1·72	1·84	1·86	1·86
CH_3Br	1·70	1·81	1·82	1·82
CH_3I	1·48	1·59	1·56	1·64*
CH_3CN	3·38	3·66	3·73	3·94–3·98
$CHCl_3$	1·10	0·99	0·99	1·01
$(CH_3)_2CO$ ..	2·74	2·85	2·86	2·89
Paraldehyde ..	1·98	1·66	1·60	1·44
C_6H_5F	1·38	1·49	1·51	1·57
C_6H_5Cl	1·58	1·74	1·69	1·73
C_6H_5Br	1·51	1·69	1·59	1·70*
C_6H_5I	1·39	1·64	1·44	1·70*
$C_6H_5NO_2$	3·95	4·42	4·18	4·24
C_6H_5CN	4·02	4·46	4·29	4·39
$C_6H_5CH_3$	0·34	0·37	0·36₅	0·37
$(CH_3)_3CCl$ ..	2·14	2·13	2·13	2·13

* Present work ; for references to other μ_{gas} (obs.) values, see Le Fèvre and Le Fèvre (1954).

We have explored the possibility of modifying the original empirical expression to avoid the occurrence of negative powers for the term $e - e^{x^2}$. The most satisfactory appears to be formula (1).

$$\frac{\mu^2_{\text{sol.}}}{\mu^2_{\text{gas}}} = 1 + \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2}[e^{x^2} - (e - e^{x^2})^{2n_2(n_1^2 - n_2^2)^2(1 - e^{x^2})^2}]. \quad \dots \quad (1)$$

Table 2 compares the applicability of the original formula and of formula (1) to the data set out by Le Fèvre and Le Fèvre (1954) in their Table 3.

Formula (1) thus covers the cases of CH_3I, C_6H_5Br, and C_6H_5I adequately enough, although it forecasts slightly less correct moments in some other cases. Considered overall however, column 3 seems a better fit to column 5 than does column 4.

One of us (D.A.A.S.N.R.) is grateful to the Commonwealth Government of Australia for a Research Fellowship awarded under the Colombo Plan.

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THE ISOLATION OF ERGOSTEROL FROM *STACHYBOTRYS ATRA CORDA**

By R. THOMAS†

During an investigation of the cellulose metabolism of the mould *Stachybotrys atra* Corda, a colourless crystalline solid with properties closely resembling those of ergosterol was isolated in low yield from the mycelium of a cellulose culture. A further quantity of the same product was isolated from a sample of mycelium grown on starch medium. Repeated crystallization yielded a pure product, the melting point of which was not depressed on admixture with an authentic sample of ergosterol. This identity was confirmed by comparing their specific optical rotations and infra-red spectra.

No metabolic product of the genus *Stachybotrys* has been previously described ; however, the demonstration of ergosterol as a mycelial constituent

of *S. atra* is in accordance with its previous isolation from many yeasts and lower fungi (Bills and Honeywell 1928.; Birkinshaw, Callow, and Fischmann 1931 ; Ottke 1949).

Experimental

The melting points are uncorrected.

The mould was grown at 28 °C in submerged culture on a modified Waksman-Carey medium (Jermyn 1953) ; biotin was an essential growth factor.

After 12 days' growth on a 1% cellulose medium, the cellulose-mycelium residue (c. 20% mycelium) was washed, dried in a forced draught oven at 50 °C, and 28 g of the finely ground mixture extracted with light petroleum (b.p. 40–60 °C) in a Soxhlet apparatus for 24 hr. It was then further extracted with ether for 20 hr. The light petroleum extract yielded an orange waxy product (0·37 g) containing a crystalline residue. The crystals were separated by washing with light petroleum ; the residue consisted of colourless needles (0·040 g), m.p. 135–148 °C, which were insoluble in hot 2N sodium hydroxide, but soluble in hot benzene, chloroform, and ethanol. In concentrated sulphuric acid they dissolved forming a bright orange solution. The ether Soxhlet extract on concentration yielded a pale yellow gum (0·68 g) which could not be induced to crystallize.

The mycelium from a 5 day culture on 1% starch medium was washed, dried, and extracted with light petroleum and ether as above. The light petroleum extract yielded an oil (0·70 g from 40 g of mycelium) which partially crystallized on trituration with light petroleum, yielding colourless needles (0·110 g), m.p. 150–153 °C with properties closely parallel to those of the corresponding product from the cellulose-mycelium mixture. The ether extract consisted of a yellow oil (0·41 g) containing some crystalline material. The crystals were isolated and proved to be identical with those of the light petroleum extract (0·045 g). The combined yield was 0·155 g from 40 g of mycelium, that is, 0·4%. Purification was effected by repeated crystallization from ethanol-benzene mixture (2 : 1) ; the final product consisted of colourless plates (0·012 g), m.p. 158–159 °C ; $[\alpha]_D^{20}$ —129° (c, 2·387 in CHCl$_3$).

An authentic sample of ergosterol recrystallized in an identical manner ; $[\alpha]_D^{20}$ —128° (c, 2·010 in CHCl$_3$) and m.p. 158 °C not depressed on admixture with the mycelium product. Both substances gave identical colour sequences in chloroform on addition of glacial acetic acid and concentrated sulphuric acid (Liebermann-Burchard reaction). When examined in a Perkin-Elmer spectrometer (model 12C) as a " Nujol "-mull, the two specimens possessed identical infra-red spectra over the range 650 to 1350 cm^{-1}.

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THE USE OF MANNICH BASE METHIODIDES IN THE DIENE REACTION*

By A. J. Birch† and M. Slaytor†

Mannich base methiodides (e.g. I) have been extensively used in Michael reactions as sources of vinyl ketones in order to avoid handling and keeping these usually unstable compounds (see, for example, du Feu, McQuillin, and Robinson 1937). Mannich bases themselves have been used in two instances as sources of dienophiles in Diels-Alder reactions (Jacquier and Boyer 1953) and we now report some parallel work using the methiodides (I, R=CH₃ or Ph) with 2,3-dimethylbutadiene. With (I, R=CH₃) 4-acetyl-1,2-dimethyl*cyclo*hexene was obtained in 67 per cent. yield, compared with 75 per cent. yield from methyl vinyl ketone itself (Petrov 1941). With (I, R=Ph) 4-benzoyl-1,2-dimethyl*cyclo*hexene was obtained in 50 per cent. yield. Under somewhat different conditions Bell *et al.* (1940) obtained 35 per cent. yield based on diene from phenyl vinyl ketone. The method would appear to be generally applicable, since vinyl ketones are frequently prepared through the Mannich bases.

$$RCOCH_2CH_2\overset{+}{N}MeEt_2I^-$$

(I)
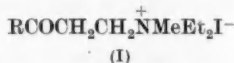
Experimental

Melting points are uncorrected.

*4-Acetyl-1,2-dimethyl*cyclo*hexene.*—2,3-Dimethylbutadiene (1 mole), the methiodide from diethylaminobutan-3-one (1 mole), and a little methylene blue were heated in a sealed glass tube to 140 °C for 8 hr. The ether-soluble portion of the product was distilled to give 4-acetyl-1,2-dimethyl*cyclo*hexene, b.p. 150 °C/60 mm (yield 67%), semicarbazone, m.p. 176 °C (Found: C, 63·1; H, 9·1%). Calc. for $C_{11}H_{18}ON_3$: C, 63·1; H, 9·1%). Petrov (1941) gives m.p. 181–182 °C for this derivative.

*4-Benzoyl-1,2-dimethyl*cyclo*hexene.*—3-Diethylamino-1-phenylpropanone similarly gave rise at 110 °C for 24 hr to 4-benzoyl-1,2-dimethyl*cyclo*hexene (50%), b.p. 188 °C/20 mm, 2,4-dinitrophenylhydrazone, m.p. 148–149 °C (Found: C, 63·4; H, 5·5% . Calc. for $C_{21}H_{22}O_4N_4$: C, 63·9; H, 5·6%). Bell *et al.* (1940) give m.p. 152 °C for this derivative.

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THE LANTHANON CONTENT OF SOUTH PACIFIC PHOSPHORITES*

By R. C. VICKERY†

The addition to superphosphate fertilizers of " trace " elements (Co, Cu, Mo, Zn, etc.) is a feature of current agronomic practice but since the early work of Hill, Marshall, and Jacob (1932) and Hill and Rader (1935, 1938) little attention appears to have been paid to the dissemination of such minor elements as occur naturally in the parent phosphorite used in manufacture of the fertilizer. Since phosphorite from Ocean and Nauru Islands in the South Pacific Ocean is the source of a large portion of the superphosphate prepared in Australia, determination of its lanthanon content was considered of interest not only to geochemists but also to agronomists.

The relationship of phosphorite to apatite has been well resolved (Clarke 1924 ; Jacob *et al.* 1933 ; Mansfield 1940) and, although in some instances it is to be expected that the genetic relationship of the lanthanons to phosphorite should resemble that to apatite, biological factors attending several phosphorite deposits must exert some differential effect upon this relationship.

Waring and Mela (1953) found $0 \cdot 02$–$0 \cdot 03$ per cent. Ln_2O_3 in some American phosphorites, but the individual lanthanon distribution reported for these occurrences was quite different from normal apatite-type assemblages (Fig. 1). Some concentration of the potentially bivalent lanthanons—samarium, europium, and ytterbium—might reasonably be expected in such a chalcophilic rock, but this was not fully substantiated. The relatively high concentration of yttrium found (30–40 per cent. of the La_2O_3 content and c. twice the Nd_2O_3 content) might argue for the coexistence of two mineral lanthanon species, for example, monazite and xenotime, but this is not in accord with the high lanthanum and low cerium contents.

Phosphate rock from Ocean and Nauru Islands has now been found to contain respectively $5 \cdot 5 \times 10^{-3}$ and nil per cent. Ln_2O_3. Distribution of the lanthanons in the former occurrence is, as far as can be determined, in good agreement with the normal apatite type (Fig. 1).

Distribution of light lanthanons in Ocean Island phosphorite ($\% Ln_2O_3 \times 10^{-4}$) :

La	Ce	Pr	Nd	Sm
$8 \cdot 25$	$19 \cdot 0$	$6 \cdot 05$	$15 \cdot 4$	$5 \cdot 5$

The presence of scandium might be expected in phosphate deposits of marine origin even in the absence of heavy lanthanons (Vickery 1955), but insufficient quantities of rare earth oxides were available to permit a search for this element.

With indications that Ocean Island and American phosphorites are of the same paragenesis but different age—Post Cretaceous *v.* Permian (Ellis 1935 ; Waggaman 1952)—it is difficult to derive reasons for the gross variation in distribution of the lanthanon content. Similarly, the difference in lanthanon contents of Nauru and Ocean Island phosphorites is inconsistent with their otherwise general chemical similarity. However, the physical nature of phosphorites from these proximate sources is sufficiently distinct to suggest the possibility of metamorphism in the Nauru phosphorite which would play its part also in minor chemical differentiation.

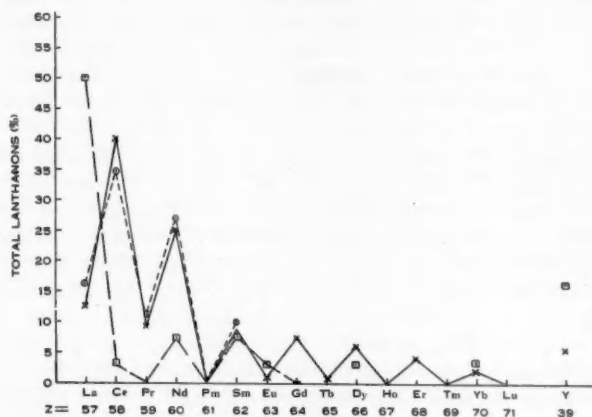Further studies on phosphorites of various origin might aid in clarifying the situation.

Fig. 1.—Lanthanon distribution of phosphorites.

x——x   Apatite-type distribution (Goldschmidt and Thomassen 1924).
□——□   Distribution given by Waring and Mela (1953).
⊙——⊙   Present paper.

Experimental

After sampling down from 7000 ton shipments, samples of Ocean and Nauru phosphate rock were reduced to 200 mesh size, and two 1 kg samples from each source decomposed by sifting into hot 50 per cent. nitric acid. Carbonate and fluoapatite present necessitated a slow rate of addition to avoid loss of material by effervescence. Residues containing organic matter were removed by centrifuging, decomposed with sulphuric acid, digested with strong sodium hydroxide solution, and finally dissolved in nitric acid. These secondary solutions were combined with those initially obtained and each was diluted to 4 l. One solution of each rock was a control and to each was added $0\cdot25$ g Ln_2O_3 (mixed oxides derived from monazite from which cerium had been eliminated). To each of the solutions at 80 °C, 300 g oxalic acid was added with strong agitation. Even at the pH attained $(2\cdot5-3\cdot0)$ much calcium oxalate precipitated but this was considered advantageous rather than otherwise, the

calcium functioning as a carrier and helping to avoid the retention of lanthanons in solution by the ferroso-oxalato complex formed with the iron in solution (Vickery 1953). Apart from contamination by calcium, overall recovery of lanthanons from solutions containing much calcium is good. This was indicated by Waring and Mela (*loc. cit.*) and confirmed by the control solutions which, in this instance, gave lanthanon recoveries of *c*. 96 per cent.

The initial oxalate precipitates containing much calcium and phosphate were ignited at a low temperature and redissolved in nitric acid. Two precipitations as hydroxide were then followed by another oxalate precipitation. This oxalate, still retaining some calcium, was ignited to oxide, dissolved in hydrochloric acid, the solution evaporated to dryness, reconstituted in 5% HCl, the solution filtered, and the lanthanons finally precipitated from a volume of 100 ml by excess oxalic acid.

The final solution from Nauru phosphate yielded no oxalate precipitate even after standing at *c*. 20 °C for 2 weeks. The control solution, containing added lanthanon ($0 \cdot 025\%$) gave 95 per cent. recovery after standing for the same period. The final solution from the Ocean Island sample yielded 55 mg Ln_2O_3 which showed no indication of calcium by the flame test. Assuming this quantity of lanthanon oxide to represent complete recovery of the natural lanthanon content, the control solution gave $96 \cdot 7\%$ recovery of the added lanthanons. The 55 mg Ln_2O_3 recovered from 1 kg of Ocean Island phosphorite represents therefore an Ln_2O_3 content of $5 \cdot 5 \times 10^{-3}$ per cent. in this rock.

Employing the data given by Moeller and Brantley (1950), distribution of individual lanthanons was determined as far as possible on a Beckman D.U. spectrophotometer. Cerium was determined by titration after oxidation with ammonium persulphate. Determination only of Ce, Pr, Nd, and Sm could thus be obtained, but an admittedly crude value of 15 per cent. of total lanthanons was obtained for La_2O_3 by utilizing the ammonium nitrate fusion technique (Vickery 1949). Summation of determined values showed that the heavy lanthanon and yttrium contents could not together be greater than $2 \cdot 5$ per cent. of total lanthanons. No indications of dysprosium or erbium were found spectrophotometrically and since the " average atomic weight " for the oxides was $143 \cdot 5$, the presence of more than 1 per cent. Y_2O_3 is doubtful. Individual values obtained and the distribution curve are given above and in Figure 1.

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